

SOME THERMODYNAMIC PROPERTIES OF AIR
AND OF CARBON DIOXIDE

BY
ARCHIE G. WORTHING

A THESIS
SUBMITTED TO THE FACULTY OF THE DEPARTMENT
OF LITERATURE, SCIENCES, AND THE ARTS OF
THE UNIVERSITY OF MICHIGAN FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

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I. INTRODUCTION.

GAY-LUSSAC¹ was the first to investigate the question as to whether or not the internal energy of a mass of gas is a function of its volume. He was not able to conclude that the internal energy was a function of the volume. On Gay-Lussac's work R. Mayer² based his computations for the mechanical equivalent of heat. Joule³ with somewhat greater care and with a modified method came to the same conclusion. In each of these experiments, the gas under consideration was allowed to expand freely, that is without the performance of external work and without the addition or subtraction of heat. This latter condition was only imperfectly realized. The question as to whether or not the internal energy of the gas was a function of the volume depended directly on whether or not the freely expanding mass of gas taken as a whole suffered any change in temperature. The ratio of such a change in temperature to the change in pressure for small changes in pressure is called the free-expansion effect. Later repetitions of Joule's experiment by Regnault⁵ and by Hirn⁶ led to the same result. Cazin⁷ about 1870 sought to do away with errors due to heating. He noted the variations with time of a fluctuating liquid pressure gauge one side of which was connected to the chamber containing the gas under experimentation. Cazin concluded that the internal energy of a gas was a function of its volume and obtained values therefor which will be noted later. Due to the use of extended extrapolations and the presence of heating effects in the stop-cock separating his two chambers initially, the results are of doubtful significance. The writer is in receipt of a letter from Professor R. A. Millikan, in which he states that he has tried a method differing

from Cazin's in that the fluctuations of the liquid in the pressure gauge were eliminated by a null method. He was not able, however, to eliminate the heating effects at the stop-cock.

The method first successfully employed was due to Joule and Thomson⁹ (Lord Kelvin). Their celebrated porous plug experiments gave consistent results, which only needed corrections for external work done by the gas in the expansion in order to show the dependency of the internal energy of the gas upon the volume. The physical quantity (μ) determined by them was the ratio of the change in temperature to the change in pressure for small changes of pressures occurring as the gas passed through the porous plug. This quantity has since received the name Joule-Thomson effect or Joule-Kelvin effect. For moderate pressures they found μ independent of the pressure and dependent on the temperature as shown in (1),

$$(1) \qquad \mu = A/\theta^2.$$

Rose-Innes,¹⁰ D. Berthelot¹¹ and Buckingham¹² have given other equations for representing the same effect.

Natanson,¹³ working with CO₂ under higher pressures, found a noticeable though small diminution in the Joule-Kelvin effect for increased pressures. Kester,¹⁴ working with CO₂ under still greater pressures, did not find this change due to the change in pressure. Rudge¹⁵ has recently made some rough determinations for CO₂ with a modified method, in which the gas escapes from a pierced bulb in a calorimeter, through a long piece of narrow tubing. His results as a whole are in agreement with those of the previous experiments mentioned. Recently Dalton,¹⁶ working with air, has found an effect similar to that found by Natanson for CO₂. Witkowski,¹⁷ having in view the applications to liquid air machines, applied thermodynamic formulæ to a great many experimentally determined results. He computed by graphical methods a series of curves which were drawn on a pressure-temperature diagram, the slopes of which at any point give directly for that point the Joule-Kelvin and the free-expansion effects. Many steps are involved in reaching the final results, and confirmation is needed for this highly important work. Searle,⁸ making use of Van der Waal's equation and assuming the constancy of the isometric heat capacity, computed for CO₂ the change in temperature for the gas expanding from a pressure of 10 atmos. to 5 atmos. Some of the results of these investigations will be noted later.

The present paper is the immediate outcome of an attempt to better comprehend the dependency of the ratio of the two heat capacities of a substance γ on its pressure and temperature. It has led to the develop-

ment of a certain thermodynamical equation which relates the ratio γ to the free-expansion effect. This together with another well-known relation for the Joule-Kelvin effect has been used in computing these effects for air and CO_2 . There existed what seemed to be satisfactory data for air. An experimental study of γ for CO_2 was undertaken in this connection to complete what seemed necessary data for that gas.

II. DERIVATION OF FORMULÆ RELATING THE RATIO γ TO THE FREE-EXPANSION AND THE JOULE-KELVIN EFFECTS.

For convenience there is given in Table I. the symbols and the units of some of the quantities used in this discussion.

Definitions of N. V. Unit, T. N. V. Unit, μ and η .—The “normal volume unit” (N. V. unit) of a substance is defined by K. Onnes²⁵ as the volume actually occupied at 0°C . by one gram-molecule of the substance when under a pressure of one atmosphere. The “theoretical normal volume unit” (T. N. V. unit) is defined as the volume that would

TABLE I.

Symbols and units of some of the quantities used.

Quantity.	Symbol.	Unit.
Pressure,	p	atmosphere.
Specific volume,	v	$\frac{\text{N. V. unit}}{\text{gr. mol.}}, \frac{\text{T. N. V. unit}}{\text{gr. mol.}}$
Temperature,	T	degree Centigrade.
Thermodynamic temperature,	θ	degree Kelvin.
Time,	t	second.
Reduced pressure,	π	critical pressure.
Reduced temperature,	τ	critical temperature.
Reduced specific volume,	ν	critical specific volume.
Quantity of heat,	Q	atmo. $\times$ N. V. unit.
Specific internal energy,	ϵ	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.}}$
Isopiestic heat capacity,	C_p	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}}, \frac{\text{calories}}{\text{gr.} \times \text{deg.}}$
Isometric heat capacity,	C_v	$\frac{\text{atmo.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}}, \frac{\text{calories}}{\text{gr.} \times \text{deg.}}$
Ratio of the two heat capacities,	γ	
Internal work in infinitesimal, reversible, isothermal expansions,	ΔW_1	atmo. $\times$ N. V. unit.
External work in infinitesimal, reversible, isothermal expansions,	ΔW_2	atmo. $\times$ N. V. unit.
Free-expansion effect,	η	$\frac{\text{deg.}}{\text{atmo.}}$
Joule-Kelvin effect,	μ	$\frac{\text{deg.}}{\text{atmo.}}$

be occupied at 0°C. by one gram-molecule of the substance under a pressure of 1 atmosphere if the gas obeyed Boyle's Law. It is assumed that the value of the product pv in such a case is the value of pv which may be obtained by extrapolation to zero pressure when considering the behavior of the actual gas. The measuring of volume in such units requires that C_p , C_v and ϵ be expressed in the units given in Table I. instead of the common units of cal./ $(\text{gr.} \times \text{deg.})$ and cal./gram. The free-expansion effect, η , of a substance, as used here, is the limiting value of the ratio of the change in temperature to the change in pressure, as the change in pressure approaches zero, for the adiabatic expansion of the substance into a vacuum. Mathematically it is

$$(2) \quad \eta = (\partial\theta/\partial p)_\epsilon.$$

The Joule-Kelvin effect, μ , as used here, is the limiting value of the ratio of the change in temperature to the change in pressure, as the change in pressure approaches zero, for the adiabatic expansion of the substance through an orifice or a porous plug from one maintained pressure to another maintained pressure. Mathematically it is

$$(3) \quad \mu = (\partial\theta/\partial p)_{\epsilon+pv}.$$

For the sake of accuracy in the theoretical discussions, it has been necessary to express temperature in the units of the thermodynamic scale. For other purposes it makes but little difference in the present work whether temperatures are measured in this scale or in the more common

centigrade scale. In the adapting of experimental data, the writer has assumed that the degree Kelvin and the degree centigrade were equal.

Derivation of Equation Relating η and γ .—The equation relating η , the free-expansion effect, to γ , the ratio of the two heat capacities may be readily obtained. Consider changes in ϵ , the internal energy of

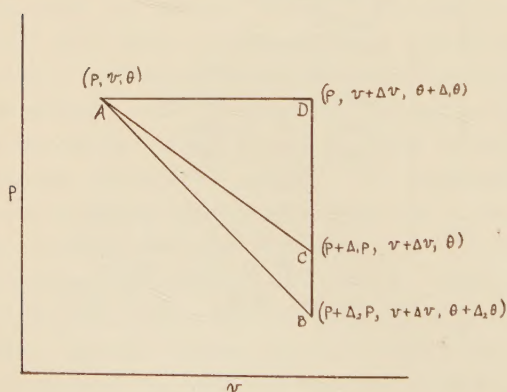


Fig. 1.

the substance under consideration, for transformations indicated in Fig. 1. Let the change represented by the straight line AB be an infinitesimal transformation in which there is no change in the specific internal energy ϵ ,

an infinitesimal free-expansion. Let the changes represented by AD , DB and AC be respectively infinitesimal isopiestic, isometric and isothermal transformations. Due to carrying the substance around the cycle $ABDA$, no resultant change occurs in ϵ . Consequently the individual changes in ϵ occurring in the individual transformation making up the cycle must sum up to zero. Moreover, since there are no changes in ϵ along AB , the changes in ϵ in passing along BD and DA must sum up to zero. Hence

$$(4) \quad C_v(\Delta_1\theta - \Delta_2\theta) - C_p\Delta_1\theta + p\Delta v = 0.$$

Since the transformations are infinitesimal, we have

$$(5) \quad \Delta_1\theta = \frac{\Delta_1\theta}{\Delta v} \Delta v = \left(\frac{\partial\theta}{\partial v} \right)_p \Delta v,$$

and

$$(6) \quad \begin{aligned} \Delta_2\theta &= \frac{\Delta_2\theta}{\Delta_2p} \frac{\Delta_2p}{\Delta v} \Delta v = \left(\frac{\partial\theta}{\partial p} \right)_\epsilon \left(\frac{\partial p}{\partial v} \right)_\epsilon \Delta v. \\ &= \eta \left(\frac{\partial p}{\partial v} \right)_\epsilon \Delta v. \end{aligned}$$

Eliminating $\Delta_1\theta$, $\Delta_2\theta$ and Δv from (4), we have

$$(7) \quad (C_p - C_v) \left(\frac{\partial\theta}{\partial v} \right)_p - p + \eta C_v \left(\frac{\partial p}{\partial v} \right)_\epsilon = 0.$$

An expression for $(\partial p/\partial v)_\epsilon$ may be obtained as follows. For all transformations we have

$$(8) \quad dp = \left(\frac{\partial p}{\partial\theta} \right)_v d\theta + \left(\frac{\partial p}{\partial v} \right)_\theta dv.$$

Hence

$$(9) \quad 1 = \left(\frac{\partial p}{\partial\theta} \right)_v \frac{d\theta}{dp} + \left(\frac{\partial p}{\partial v} \right)_\theta \frac{dv}{dp}.$$

For a free-expansion (9) becomes

$$(10) \quad 1 = \left(\frac{\partial p}{\partial\theta} \right)_v \left(\frac{\partial\theta}{\partial p} \right)_\epsilon + \left(\frac{\partial p}{\partial v} \right)_\theta \left(\frac{\partial v}{\partial p} \right)_\epsilon,$$

or

$$(11) \quad \left(\frac{\partial p}{\partial v} \right)_\epsilon = \frac{\left(\frac{\partial p}{\partial v} \right)_\theta}{1 - \eta \left(\frac{\partial p}{\partial\theta} \right)_v}.$$

The elimination of $(\partial p/\partial v)_e$ from (7) and (11) gives

$$(12) \quad \gamma = \frac{C_p}{C_v} = 1 + \frac{p}{C_v} \left(\frac{\partial v}{\partial \theta} \right)_p + \frac{\eta \left(\frac{\partial p}{\partial \theta} \right)_v}{1 - \eta \left(\frac{\partial p}{\partial \theta} \right)_v}.$$

The expressions for γ usually derived in text-books on physics are equivalent to the first two terms of the right-hand member of (12). By means of it and of certain assumptions regarding the application of the kinetic theory of gases, it is shown that for cases where such assumptions are realized the limiting values of γ are 1 and $1\frac{2}{3}$. Equation (12), however, is a perfectly general expression. It reduces to the more common expression for small pressures where $(\partial p/\partial \theta)_v$ is small and the term containing η may be disregarded. The writer has not seen elsewhere any expression similar to (12).

Equation (12), when combined with the following well-known relation deduced in texts on thermodynamics

$$(13) \quad C_p - C_v = \theta \left(\frac{\partial p}{\partial \theta} \right)_v \left(\frac{\partial v}{\partial \theta} \right)_p,$$

gives

$$(14) \quad \eta = \frac{\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p}{\frac{\gamma}{\gamma - 1} \theta \left(\frac{\partial p}{\partial \theta} \right)_v - p} \left(\frac{\partial \theta}{\partial p} \right)_v.$$

Expression of μ as a function of γ .—In texts on thermodynamics the following equation for the Joule-Kelvin effect is derived:

$$(15) \quad \mu = \frac{\theta \left(\frac{\partial v}{\partial \theta} \right)_p - v}{C_p}.$$

Equations (13) and (15) lead directly to the following

$$(16) \quad \mu = \frac{\gamma - 1}{\gamma} \frac{\theta - v \left(\frac{\partial \theta}{\partial v} \right)_p}{\theta \left(\frac{\partial p}{\partial \theta} \right)_v}.$$

Equations (14) and (16) are the two relations, the application of which form certain of the main subdivisions of this paper.

III. THE FREE-EXPANSION AND JOULE-KELVIN EFFECTS IN AIR.

Inspection of Available Data.—In order to apply equations (14) and (16), there are needed experimental data regarding γ , the interrelations of p , v , θ and their partial derivatives $(\partial p/\partial \theta)_v$ and $(\partial v/\partial \theta)_p$. γ for air may be obtained from data by Witkowski,²⁶ by Koch,²⁴ or from data by Joly²⁷ and Lussana.²⁸ Witkowski first computed C_p and C_v and then γ . C_p was obtained from the relation

$$(17) \quad \left(\frac{\partial C_p}{\partial p} \right)_\theta = -\theta \left(\frac{\partial^2 v}{\partial \theta^2} \right)_p.$$

C_v was obtained by means of (13). Values of γ were then computed for various temperatures ranging from 0°C. to -140°C. , and for pressures up to about 130 atmospheres. Later by Kundt's velocity of sound method, he measured γ directly under pressures up to 100 atmospheres and at 0°C. and -78.5°C. These results, though noticeably higher, agree quite well with the computed results, as may be seen by an inspection of Table II. Koch's results were likewise obtained by Kundt's velocity of sound method. In his experiments the pressure varied from 1 to 200 atmospheres. The temperatures were 0°C. and -79.3°C. His results agree well with Witkowski's. Joly determined C_v for air by means of his well-known, differential, steam-calorimeter method for various temperature intervals all above 0°C. and for pressures up to about 100 atmospheres. Average values of C_p for air were determined by Lussana for various intervals of temperature between 0°C. and 200°C. and for various pressures up to 100 atmospheres. These values of C_v and C_p and the values of $(\partial v/\partial \theta)_p$ and $(\partial p/\partial \theta)_v$ obtained by Amagat from his experiments on the compressibility of air, have been shown by Amagat to be quite inconsistent with one another. Data by Joly and Lussana have therefore not been relied upon in this work. The writer has seen only an abstract of Witkowski's paper in which the Kundt method of measuring γ was detailed. For the above reasons and for the added reason that the data by Koch seemed to have been obtained with great care, Koch's data have been used in the following computations. The values obtained from Koch's paper are to be found in Table II., column 7.

For the determination of the interrelations of p , v , and θ and the partial derivatives $(\partial v/\partial \theta)_p$ and $(\partial p/\partial \theta)_v$, there exist the works of Amagat,²⁹ Witkowski¹⁷ and Koch²⁴. Amagat's data relate to temperatures above 0°C. and can not be used in connection with the data on γ selected. Witkowski's results on the compressibility of air cover the range of temperatures and pressures of the γ data selected. Moreover, the values of the product $p v$ as a function of p at 0°C. and -78.5°C. have been

fairly well verified by Koch. Witkowski's data on the compressibility of air have therefore been made use of.

Method of Handling p, v, θ data.—In applying equations (14) and (16), $(\partial v/\partial \theta)_p$ and $(\partial p/\partial \theta)_v$ do not merely appear by themselves but also in the expressions $v(\partial \theta/\partial v)_p$ and $\theta(\partial p/\partial \theta)_v$. The values for these expressions were obtained as follows: Consider

$$(18) \quad (pv)_\theta = f(p).$$

The derivation of (18) with respect to p gives on rearranging

$$(19) \quad \left(\frac{\partial p}{\partial v}\right)_\theta = -\frac{p}{v - f'(p)}.$$

Likewise we may consider

$$(20) \quad (v)_p = F(\theta).$$

Whence

$$(21) \quad \left(\frac{\partial v}{\partial \theta}\right)_p = F'(\theta),$$

and

$$(22) \quad v \left(\frac{\partial \theta}{\partial v}\right)_p = \frac{F(\theta)}{F'(\theta)}.$$

Since

$$(23) \quad \left(\frac{\partial p}{\partial \theta}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_\theta \left(\frac{\partial v}{\partial \theta}\right)_p,$$

$$(24) \quad \theta \left(\frac{\partial p}{\partial \theta}\right)_v = \frac{p\theta F'(\theta)}{v - f'(p)}.$$

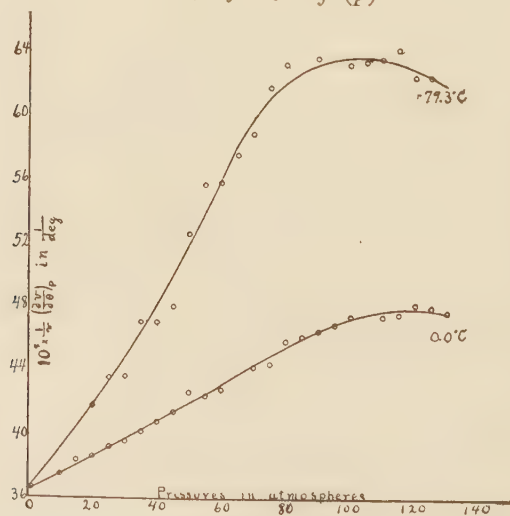


Fig. 2.

Variation of $\frac{1}{v} \left(\frac{\partial v}{\partial \theta}\right)_p$ with pressure for air.

For air at various pressures and at 0° C. and - 79.3° C., $f'(p)$ and $F'(\theta)$ were obtained from Witkowski's data by graphical means. The individual values of the reciprocals of $v(\partial\theta/\partial v)_p$ which were obtained together with the smoothed curves are shown in Fig. 2. The values used were taken from these curves.

Results from Data by Witkowski and Koch.—Certain data and computations leading to the values of μ and η are included in Table II. The

TABLE II.

Computations for μ and η of air using data obtained by Witkowski and by Koch. Air at 0° C.

p	pv	$\log \left[- \left(\frac{\partial p}{\partial v} \right)_{\theta} \right]$	$\log \left(\frac{\partial v}{\partial \theta} \right)_p$	$\theta - v \left(\frac{\partial \theta}{\partial v} \right)_p$	$\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p$	γ	μ	η	$\frac{\Delta W_1}{\Delta W_2}$
10	.9951	1.9997	4.5737	7.7	.23	1.435	.228	.259	.023
15	.9923	2.3519	.4026	11.4	.52	1.448	.227	.260	.035
20	.9897	2.6017	.2824	15.0	.92	1.460	.226	.259	.046
25	.9869	2.7958	.1906	18.6	1.48	1.472	.225	.265	.059
30	.9842	2.9546	.1160	22.0	2.13	1.483	.223	.263	.071
40	.9793	3.2057	.0005	28.7	3.92	1.508	.220	.270	.090
50	.9754	3.4010	5.9134	35.1	6.35	1.533	.217	.275	.127
60	.9723	3.5614	.8440	41.2	9.48	1.557	.212	.278	.158
70	.9701	3.6969	.7881	47.0	13.46	1.582	.207	.281	.192
80	.9688	3.8160	.7392	52.5	18.10	1.603	.201	.279	.226
90	.9681	3.9212	.6984	57.7	23.8	1.625	.195	.278	.264
100	.9681	4.0155	.6598	61.3	29.4	1.645	.186	.270	.294
110	.9690	4.1034	.6244	64.0	36.0	1.663	.175	.263	.327
120	.9710	4.1838	.5882	64.5	41.6	1.682	.162	.253	.347
130	.9738	4.2602	.5530	63.6	47.7	1.700	.147	.243	.367

Air at - 79.3° C.

1	.708	.1488	3.5643	.8		1.405	.230		
10	.690	2.1500	4.5866	15.1	.57	1.463	.452	.447	.057
15	.681	2.5022	.4236	22.6	1.34	1.495	.458	.463	.089
20	.672	2.7520	.3124	30.1	2.48	1.530	.464	.476	.124
25	.664	2.9459	.2299	37.4	4.05	1.567	.466	.489	.162
30	.655	3.1046	.1644	44.3	6.01	1.602	.462	.492	.200
40	.638	3.3541	.0664	56.9	11.04	1.681	.452	.487	.276
50	.620	3.5483	.0062	71.6	19.48	1.765	.447	.493	.390
60	.606	3.7071	5.9554	81.9	29.01	1.857	.424	.474	.483
70	.587	3.8499	.9209	93.1	44.4	1.950	.397	.457	.634
80	.573	3.9819	.8783	99.0	60.5	2.044	.360	.431	.756
90	.562	4.0981	.8340	102.3	75.8	2.125	.327	.397	.842
100	.554	4.2097	.7900	104.0	93.7	2.200	.293	.368	.937
110	.550	4.3122	.7478	104.4	112.5	2.290	.264	.344	1.023
120	.547	4.3998	.7072	104.3	128.0	2.370	.243	.324	1.067
130	.546	4.4804	.6683	103.7	143.0	2.460	.226	.308	1.100

p is expressed in atmos., v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, and μ and η in $\frac{\text{deg.}}{\text{atmo.}}$.

value of the ice point for this table was taken as 273.2° K. The value used for the other and later computation was 273.1° K. The variations produced by not using the latter value throughout are inappreciable, hence Table II. has not been corrected in this respect. The computed free-expansion and Joule-Kelvin effects are indicated in Fig. 3 by open circles.

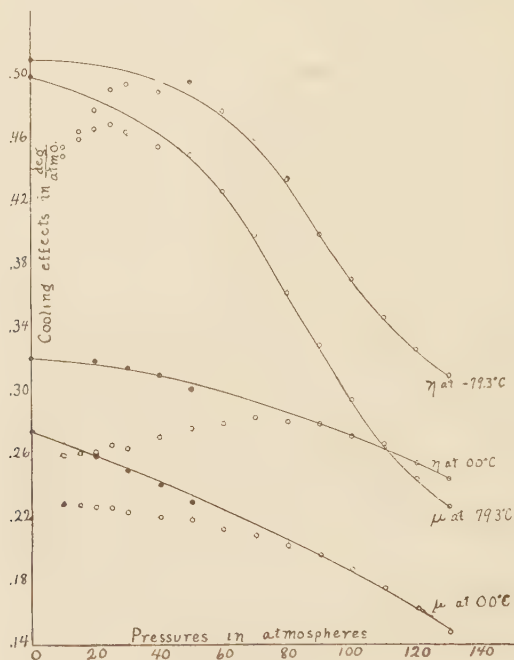


Fig. 3.

Variation with pressure of the free-expansion (η) and Joule-Kelvin (μ) effects in air at 0.0° C. and 79.3° C.

Results based on

Witkowski's data ○
K. Onnes's equation ●

K. Onnes's Equation.—The values in Fig. 3 indicated by circles with filled centers are obtained by using Kamerlingh Onnes's¹⁶ empirical equation representing the isothermals of air at 0° C., 20° C. and 99.4° C. for pressures up to about 50 atmospheres and Koch's data on γ . The equation given by Kamerlingh Onnes is

$$(25) \quad pv = A + \frac{B}{v} + \frac{C}{v^2},$$

where v is expressed in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, p in atmospheres, and A , B and C

are functions of θ , the individual values of A , B and C are as shown for the given temperatures in Table III.

TABLE III.
Constants for Kammerlingh Onnes's empirical equation for air.

T	A	B	C
0.0° C.	1.0006	−.0357440	.0529594
20.0° C.	1.0739	− 40495	30178
99.4° C.	1.3647	+ 25057	35669

Results from K. Onnes's Equation and Koch's Data.—The computations for μ and η , excepting those for zero pressure, differ in this case from those in which the p, v, θ relations were obtained from Witkowski's data in that $(\partial p/\partial v)_\theta$ was obtained in this case by differentiation. Table IV. indicates these results.

TABLE IV.
Computations for μ and η of air at 0° C. using Kammerlingh Onnes's equation of state and γ data by Koch.

p	$p v$	$\log \left[- \left(\frac{\partial p}{\partial v} \right)_\theta \right]$	$\log \left(\frac{\partial v}{\partial \theta} \right)_p$	$\theta - v \left(\frac{\partial \theta}{\partial v} \right)_p$	$\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p$	γ	μ	η	$\frac{\Delta W_1}{\Delta W_2}$
0	1.0006	—	—	—	—	—	.273	.320	.000
10	.9952	2.0000	4.5759	8.9	.29	1.435	.262	.322	.029
20	.9902	2.6022	.2869	17.3	1.16	1.448	.258	.318	.058
30	.9859	2.9550	.1220	24.9	2.62	1.460	.249	.313	.087
40	.9822	3.2060	.0073	31.7	4.64	1.472	.239	.308	.116
50	.9790	3.4009	5.9199	37.7	7.18	1.483	.229	.300	.144

p is expressed in atmos., v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$, and μ and η in $\frac{\text{deg.}}{\text{atmo.}}$.

Values for μ and η at Zero Pressure.—The values for μ_0 and η_0 at $p = 0$ were obtained by a method indicated for μ_0 by J. P. Dalton.¹⁶ The method of obtaining η_0 is outlined briefly here. By means of (13), (14) may be rewritten as

(26)

$$\eta = \frac{\theta - p \left(\frac{\partial \theta}{\partial p} \right)_v}{C_p \left(\frac{\partial \theta}{\partial v} \right)_p - p}$$

By the direct processes of calculus and by the substitution of $v = \infty$, we get

(27)

$$\eta_0 = \frac{1}{C_{p0} - \frac{\partial A}{\partial \theta}} \frac{\theta \left(\frac{\partial B}{\partial \theta} \right) - B}{A}$$

The analogous value for μ_0 obtained from (15) is

$$(28) \quad \mu_0 = \frac{\theta \frac{\partial B}{\partial \theta} - 2B}{C_{p0} A}.$$

The well established value of C_{p0} for air under low pressures is very closely $.2375 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$, or in the units consistent with those chosen for p and v in this paper $.01273 \frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.} \times \text{deg.}}$.

It is to be noticed that the two sets of values for μ and η included in Tables II. and IV. differ considerably, the greatest variations occurring with the smaller pressures. This is evidently due to the smallness of the quantities $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$. The entire differences result from very small but noticeable variations in corresponding values of $(\partial v/\partial\theta)_p$. This source of uncertainty is plainly much less effective at the higher pressures.

Results for μ at 0°C .—The value obtained for the Joule-Kelvin effect at zero pressure μ_0 at 0°C . from Kamerlingh Onnes's equation agrees very closely, as has been shown by J. P. Dalton, with the experimental value obtained by Joule and Kelvin and with his own experimental value. It also agrees very well with the computed value obtained by using Buckingham's equation in which he expressed in a single formula the results of all experimental Joule-Kelvin effects for various substances under moderate pressures, as a function of the temperature. Each of these values closely approximates $.273 \frac{\text{deg.}}{\text{atmo.}}$. This value has therefore been selected on the plot Fig. 3, as the starting point for the curve at 0°C . J. P. Dalton's experimental results for the porous plug expansion of air through a glass reduction-valve are very well represented by the equation,

$$(29) \quad T_1 - T_2 = .273(p_1 - 1) - .000208(p_1^2 - 1).$$

p_1 represents the initial pressure of the air, a quantity which in his experiments reached a pressure of 43 atmospheres. T_1 the initial temperature was 0°C . The final pressure was that of the atmosphere. T_2 represents the final temperature. The ratio $\frac{T_1 - T_2}{p_1 - 1}$, if plotted on Fig. 2 would start with the same initial value for μ_0 as chosen and would continue from there in a line lying approximately half way between the line $\mu = .273 \frac{\text{atmo.}}{\text{deg.}}$ and a line passing through the points determined by

Kamerlingh Onnes's equation and the γ data of Koch. When it is remembered that the results of Dalton represent effects from finite expansion of considerable magnitude and that the mean temperatures during such expansions are, for the higher pressures especially, noticeably less than 0°C. , for which temperatures the Joule-Kelvin effect becomes greater, it will be seen that the deviation spoken of above is to be expected. Moreover, it may be readily shown that this deviation agrees in magnitude with what is obtained by some rather rough computations. For an initial pressure of 40 atmospheres, (29) gives for T_2 a value of -10.3°C. If now (1) may be taken as approximately true, and if it is further assumed that the value of μ for 0°C. and atmospheric pressure is $.273 \frac{\text{deg.}}{\text{atmo.}}$, it follows that the value of μ for -10.3°C. and atmospheric

pressure is $.294 \frac{\text{deg.}}{\text{atmo.}}$. The value for μ at 0°C. and 40 atmospheres, according to data based on Kamerlingh Onnes's equation, is $.239 \frac{\text{deg.}}{\text{atmo.}}$.

For air initially at 0°C. and 40 atmospheres, expanding through a valve as in J. P. Dalton's experiment to atmospheric pressure, an average value for μ might be expected which is near the mean of the extreme values given above. This computed average for μ , $.266 \frac{\text{deg.}}{\text{atmo.}}$, agrees

very well with the value to be obtained from (29), $.264 \frac{\text{deg.}}{\text{atmo.}}$. Because of these agreements, it has been assumed in drawing the curve for μ at 0°C. that the values computed with the aid of Kamerlingh Onnes's equation of state are correct. The general trend of these values are such as to show agreement with the values of μ obtained for the higher pressures using Witkowski's data. It might be expected that these latter values would not be far from the correct values, since here, as may be seen in Table II., small errors entering into $\theta - v(\partial\theta/\partial v)_p$ would cause but small errors in the computed results for μ . Hence the further continuance of the curve. The curve for μ at 0°C. is well represented by (30).

$$(30) \quad \mu_{T=0} = .273 - .00076p - .0000012p^2.$$

Results for μ at -79.3°C. —In drawing the curve for μ at -79.3°C. , the value given by Buckingham's equation was selected as being the most probable value for μ at zero pressure. This value of $.498 \frac{\text{deg.}}{\text{atmo.}}$ was found to agree very well with the value $.486 \frac{\text{deg.}}{\text{atmo.}}$ for -78.5°

which was obtained by using as before, equations similar to (25) and Witkowski's experimental value of C_p $.2375 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$ or $.01273 \frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$. The equations used here however were of the type

$$(31) \quad pv = A + B/v.$$

A and B have the values indicated in Table V. at the stated temperatures

TABLE V.
Constants for equation (31).

T	A	B
0.0° C.	1.0006	-.000574
- 78.5	.7130	-.001193
-103.5	.6214	-.001473

when as before p is expressed in atmospheres and v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$. The values of A and B relating to 0° C. have been given by Kamerlingh Onnes. The remaining values of A were determined on the supposition that at zero pressure air rigorously obeys the perfect gas law. The remaining values for B were determined with the additional supposition that Witkowski's data on the values of v for air at - 78.5° C. and - 103.5° C. for a pressure of 20 atmospheres are correct. These values are respectively $.03389$ and $.02848 \frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$.

Results for η at 0° C.—In drawing the curve for the free-expansion effect η of air at 0° C., preference was given at small pressures to the values computed with the aid of Kamerlingh Onnes's equation and constants, because they had given very nearly the correct results for the Joule-Kelvin effect at the same temperature and pressure. It is, of course, to be borne in mind that, even if an equation of state should indicate correct values for the Joule-Kelvin effect for any pressure and temperature, the computed free-expansion effects as determined by that equation of state might deviate far from the true values. If, however, in addition to leading to the correct Joule-Kelvin effects, the equation correctly represents the isothermals, then as has been shown by Bakker,³⁰ the equation will lead to correct free-expansion effects. As in connection with the Joule-Kelvin effect and for a similar reason, we may expect that the computed free-expansion effects based on Witkowski's data, in the case of high pressures, will not deviate far from the true values.

Here $\theta(\partial p/\partial \theta)_v - p$ is the term which practically determines the accuracy of the computed results. The writer knows of no direct determinations of η which might be used here. The curve for η at 0° C. is well represented by (32).

$$(32) \quad \eta_{T=0} = .320 - .00018p - .0000032p^2.$$

Results for η at -79.3° C.—In drawing the curve for the free-expansion effect η at -79.3° C., the value for zero pressure was chosen as follows: The value computed with the aid of equation (31) and the accompanying constants for zero pressure and -78.5° C. was $.496 \frac{\text{deg.}}{\text{atmo.}}$. Since the Joule-Kelvin effect for zero pressure and -78.5° C. computed from the same data differed by $.012 \frac{\text{deg.}}{\text{atmo.}}$ from the value given by Buckingham's equation for -79.3° C., and since the variations of μ and η with temperature seem to be about the same, as the general trend of the curves drawn indicate, it was assumed, that the value for η_0 at -79.3° C. was higher than the computed value at -78.5° C. by $.012 \frac{\text{deg.}}{\text{atmo.}}$, making the value selected $.508 \frac{\text{deg.}}{\text{atmo.}}$.

Agreement with Witkowski's Results.—There has been mentioned the work of Witkowski.¹⁷ He started with a number of experimentally determined relations between p , v and θ , and with the experimental conclusion that C_p for air at 1 atmosphere is independent of the temperature, computed isenthalpic and isenergetic curves for air embracing a region from 0° C. to -140° C. and from zero pressure to 130 atmospheres. Graphical methods were largely used. The slopes of these curves give directly the Joule-Kelvin and the free-expansion effects. The writer has included in Table VI. a number of values for μ and η thus obtained together with the corresponding values from the present work. Excepting for the lower pressures, the agreement is good. As has been previously suggested, the variations here are undoubtedly largely due to the smallness of the corresponding values for $\theta - v(\partial \theta/\partial v)_p$ and $\theta(\partial p/\partial \theta)_p - p$. Witkowski himself ascribed the variation of his results from those of Joule and Kelvin to the uncertainties entering into his graphical calculations.

Internal Work of Expansion.—It is of considerable interest in this connection to consider the relative magnitudes of the effects of the internal forces, intramolecular as well as intermolecular, which give rise to the free-expansion and to a large extent to the Joule-Kelvin effects. This

TABLE VI.

Corresponding values of μ and η according to Witkowski and to Worthing.

T in $^{\circ}\text{C.}$	Values of μ in $\frac{\text{deg.}}{\text{atmo.}}$			T in $^{\circ}\text{C.}$	Values of η in $\frac{\text{deg.}}{\text{atmo.}}$		
	$\bar{p}$ in Atmos.	(Witkowski.)	(Worthing.)		$\bar{p}$ in Atmos.	(Witkowski.)	(Worthing.)
0.0	40	.20	.242	0.0	50	.23	.303
	70	.23	.215		84	.265	.282
	113	.175	.175		121	.252	.252
-79.3	0	.515	.498	-79.3	19	.491	.505
	15	.496	.490		38	.509	.496
	30	.476	.476		55	.500	.480
	43	.468	.460		71	.468	.452
	57	.448	.430		88	.424	.403
	69	.400	.397		104	.358	.358
	83	.365	.349		122	.323	.322
	97	.308	.303				
	112	.248	.260				
	130	.222	.226				

may best be done by determining the ratio of the work done against these internal forces ΔW_1 to that done against external forces ΔW_2 when a gas undergoes an infinitesimal, reversible, isothermal expansion. The internal work for such an expansion is evidently equal to the change in internal energy, which in turn is equal to the heat, measured in appropriate units, which must be added to the substance following the free-expansion from the initial to the final volume to bring it without changing the volume to the initial temperature.

$$(33) \quad \Delta W_1 = (\Delta \epsilon)_{\theta} = -C_v \eta (\Delta p)_{\epsilon} = -C_v \eta \left(\frac{\partial p}{\partial v} \right)_{\epsilon} \Delta v.$$

With the aid of (11), (12) and (13), there follows

$$(34) \quad \Delta W_1 = \left(\frac{\partial \epsilon}{\partial v} \right)_{\theta} \Delta v = - \frac{C_v \eta \left(\frac{\partial p}{\partial v} \right)_{\theta}}{1 - \eta \left(\frac{\partial p}{\partial \theta} \right)_v} \Delta v = \left[\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p \right] \Delta v.$$

The desired ratio of the internal work to the external work is given by

$$(35) \quad \frac{\Delta W_1}{\Delta W_2} = \frac{\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p}{p}.$$

This relation is true for all infinitesimal, reversible expansions in which the accompanying changes in p are infinitesimal. Values for $\Delta W_1/\Delta W_2$

for air have been computed and are to be found in the last columns of Tables II. and IV. The results have been platted in Fig. 4. In Fig. 4 only those points have been platted for which the corresponding computed values of μ and η were found to fall closely on the platted curves of Fig. 3. What has been noted previously regarding the uncertainties in $\theta(\partial p/\partial \theta)_v - p$ at low pressures, applies equally here. The changes in $\Delta W_1/\Delta W_2$ with pressure and with temperature are very evident, the ratio for the lower temperature and the higher pressures being greater than unity.

Conclusions Regarding η , μ and $\Delta W_1/\Delta W_2$ of Air.—The plats show that in air for the region considered:

1. The free-expansion effect η is greater than the Joule-Kelvin effect μ for the same pressure and temperature.

2. The absolute difference between η and μ for the same pressure and temperature increases with increasing pressure.

3. Both η and μ are greater for the lower temperature than for the higher temperature.

4. Both η and μ beginning with low pressures, decrease with increasing pressures, the rate of decrease being the greater, the greater the pressure.

5. The ratio of the internal work to the external work for infinitesimal, reversible, isothermal expansions $\Delta W_1/\Delta W_2$ is greater at -79.3°C. for a given pressure than at 0°C.

6. The ratio $\Delta W_1/\Delta W_2$ starts with zero values at zero pressure and increases with pressure, and in the case of the lower temperature, reaches a value greater than unity.

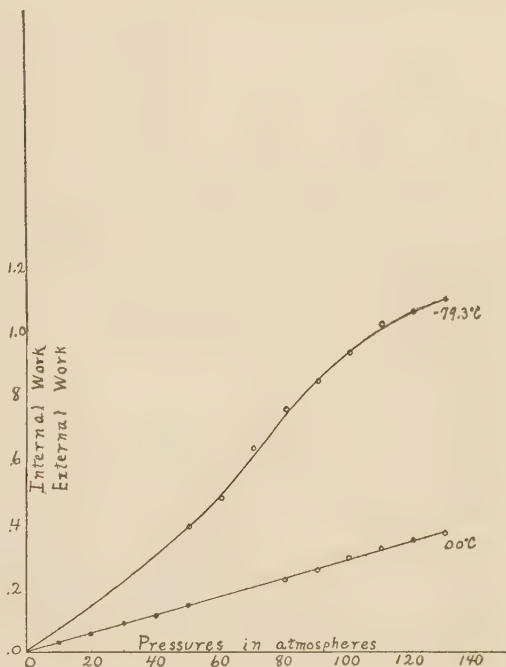


Fig. 4.

Variation with pressure of $\frac{\text{internal work}}{\text{external work}}$ in air for infinitesimal, reversible, isothermal expansions.

Results based on

Witkowski's data..... ○

K. Onnes's equation..... ●

IV. THE DETERMINATION OF γ FOR CO₂ AS A FUNCTION OF THE PRESSURE AND THE TEMPERATURE.

Consideration of Existing Data.—There exist many determinations of γ for CO₂ under atmospheric pressure. There exist for pressures considerably greater, so far as the writer knows, only the computations of Amagat,¹³ in which he combines the determinations of C_v made by Joly³² with his own determinations of the interrelations of p , v and θ . His own work enabled him to determine $\theta(\partial p/\partial \theta)_v(\partial v/\partial \theta)_p$ for the gas at any desired pressure and temperature. By the application of (13), C_p and then γ were determined; first at varying pressures for a density of the CO₂ of .124 gr./cm.³, then at varying pressures for a temperature of 50° C. He obtained various values for γ which showed that quantity to increase noticeably with increasing pressure and with decreasing temperature. For a temperature of 50° C. and a pressure of 100 atmospheres, he found γ to be 4.633. Unfortunately the results are such that it is impossible to check them by comparing them with other determined values at one atmosphere.

At about the same time there appeared papers by Lussana³³ on the values of C_p for CO₂ at about the same pressures and temperatures. Evidently his results might be combined with Amagat's, C_v determined and then γ ; or his results might be combined with Joly's directly and γ thus determined. The writer has attempted the latter. It has been necessary to plot the given values of C_p and C_v in order to get values for C_p and C_v under the same conditions. Table VII. includes the results

TABLE VII.

γ for CO₂ from data by Joly and by Lussana.

p	30°			50°			80°		
	C_p	C_v	γ	C_p	C_v	γ	C_p	C_v	γ
10	.297	.169	1.76	.259	.169	1.53	.250	.168	1.49
20	.301	.173	1.75	.263	.172	1.53	.253	.171	1.48
30	.318	.179	1.72	.268	.177	1.52	.258	.175	1.48
40	.318	.184	1.73	.276	.182	1.52	.264	.180	1.47

p is expressed in atmospheres. C_p and C_v are expressed in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

of such computations. Joly's conclusion, that for densities less than .124 gr./cm.³ C_v for CO₂ is practically independent of the temperature, was assumed as correct. There are only a few values which may be compared with those mentioned above as having been obtained by Amagat. There is but very little agreement between the two sets of

determinations. Moreover the variations of γ in Table VII. are such as would indicate values of γ under atmospheric pressure which are very different from the generally accepted values. There is evident need of further determinations of γ for CO_2 for various pressures and temperatures.

Methods of Measuring γ for Gases under High Pressures.—There are several methods of determining γ which are practicable when applied to a gas under high pressures. There are (1) the thermodynamic method used by Witkowski as described briefly in an earlier part of the present paper; (2) the separate determination of C_p and C_v ; (3) the determination of C_p and the consequent computation of C_v by equation (13); (4) the determination of C_v and the consequent determination of C_p by equation (13); (5) the method of Jamin and Richard³⁴ in which the isopiestic and isometric changes in temperature of a gas heated by a wire carrying an electric current is measured; (6) the method of Assmann,³⁵ in which there is observed the period of vibration of a system in a closed glass tube composed of a mass of the gas separated into two parts by means of a column of mercury; (7) the velocity of sound method; (8) the method of Lummer and Pringsheim³⁶ so modified as to apply to gases far removed from the state of perfect gas; and (9) the method of Maneuvrier,³⁷ a null method based on the same fundamental principles as the method commonly called after Clement and Desormes.

Reasons for Choosing the Method Selected.—The thermodynamic method of Witkowski might be applied to the data given by Amagat for CO_2 . There would be required in addition however the variations of C_p or C_v with temperature at a given pressure such as atmospheric. Such determinations as these have been made but there is a great lack of consistency in the data. It has not seemed desirable to make use of this method in the present case. The next three methods necessitate the measurement of C_p , C_v or both for various pressures and temperatures. These are very difficult undertakings. Moreover, as they have already been measured by Joly and Lussana as noted above, and with very probable, serious errors as is suggested by Table VII., none of these three methods has been used in the present work. Jamin and Richard's method would undoubtedly be hard to realize under high pressure, especially in the carrying out of an isopiestic heating. Assmann's method might well yield good results, when all allowances are made for disturbing factors. The velocity of sound method has been used by Witkowski and by Koch for air with fair agreement of results with each other and with the former's results by the thermodynamic method. This method has been criticized by J. W. Capstick,³⁸ and by J. H. Jeans,³⁹ on account of a lag in the

adjustment of the intermolecular and intramolecular energies of a gas on the passage of a sound wave through the gas. In Chapter XVI. of his "The Dynamical Theory of Gases" he concluded that any such lag in adjustment, provided that a certain supposition is true, "is in every way imperceptible." The method of Maneuvrier seemed free from this serious objection. It has been used. Practically, in Maneuvrier's method the compressions are no more reversible than those in sound experiments. Time, however, is given in this method for the practical balancing of the intramolecular and the intermolecular energies before actual measurements are made. The apparatus which was constructed for this work has been so designed as to make possible measurements according to a modification of Lummer and Pringsheim's method. However, time has not been found available for the perfection of this method, and consequently no measurements of that kind have been made.

Maneuver Method.—The method of Maneuvrier is based on a theorem due to Reech,⁴⁰ which is applicable to any substance whatever. A simple derivation of the equation expressing this theorem follows. Let AB , AC , AD and DB , Fig. 1, represent in this instance respectively infinitesimal reversible adiabatic, isothermal, isopiestic and isometric changes. Consider the change in internal energy which takes place when a substance is carried around the cycle $ADBA$. We have then

$$(36) \quad (C_p \Delta_1 \theta - p \Delta v) + C_v (\Delta_2 \theta - \Delta_1 \theta) + p \Delta v = 0.$$

The two following relations are evident.

$$(37) \quad \Delta_2 \theta = \left(\frac{\partial \theta}{\partial v} \right)_q \Delta v.$$

$$(38) \quad \Delta_1 \theta = \left(\frac{\partial \theta}{\partial v} \right)_p \Delta v.$$

There follows at once

$$(39) \quad \frac{C_p - C_v}{C_v} \left(\frac{\partial \theta}{\partial v} \right)_p = - \left(\frac{\partial \theta}{\partial v} \right)_q,$$

or

$$(40) \quad \gamma = 1 - \left(\frac{\partial v}{\partial \theta} \right)_p \left(\frac{\partial \theta}{\partial v} \right)_q.$$

By a process very similar to that involved in (8), (9) and (10), we get

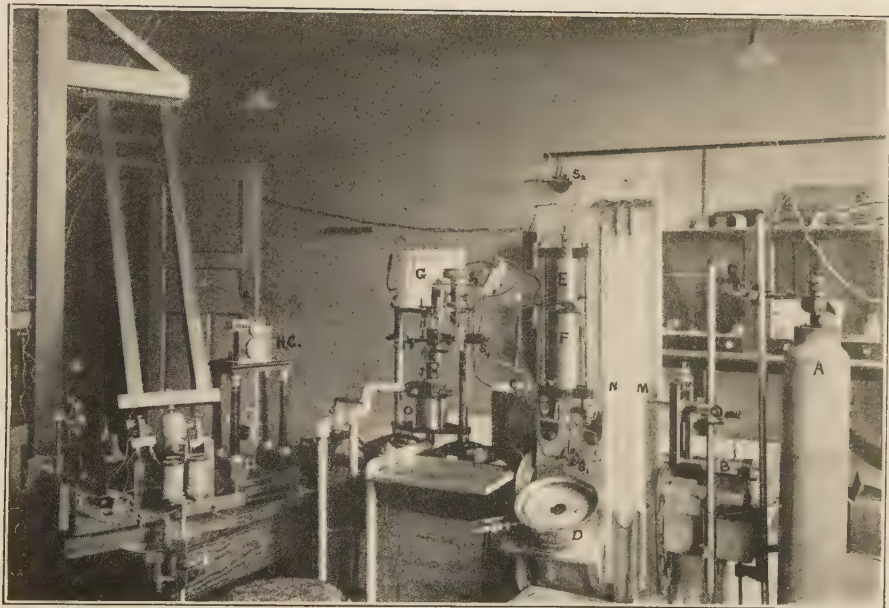
$$(41) \quad \left(\frac{\partial \theta}{\partial v} \right)_q = \left(\frac{\partial \theta}{\partial v} \right)_p + \left(\frac{\partial \theta}{\partial p} \right)_v \left(\frac{\partial p}{\partial v} \right)_q.$$

The application of (8) to an isopiestic process gives

$$(42) \quad \left(\frac{\partial v}{\partial \theta} \right)_p \left(\frac{\partial \theta}{\partial p} \right)_v = - \left(\frac{\partial v}{\partial p} \right)_\theta.$$

Apparatus.—The apparatus and the method of experimentation may be seen from an inspection of Fig. 5 (see also Plate I.) which represents the essential portions of the apparatus as finally connected and used. In general the arrangements and the materials have been so chosen as to withstand with safety pressures of 100 atmospheres though the actual

highest pressure attained in these experiments was about 57 atmospheres. *A* represents the tube containing CO_2 under pressure which in the experiments to be considered was the source of the gas and of the pressure. *B* represents a cylinder of about 250 cm.³ capacity containing phosphorous pentoxide sprinkled through cotton-wool for the purpose of removing the moisture from the gas passing through it. *C* represents a distributing chamber of about 600 cm.³ capacity which also served as a maintainer of the pressure in the protective system to be spoken of later. At the stop-cock *S*₂, the gas enters the system where it is to be experimented with. *D* is a Bourdon steam test-gauge reading to 800 $\frac{\text{lbs. wt.}}{\text{in.}^2}$ by steps of 5 $\frac{\text{lbs. wt.}}{\text{in.}^2}$. *E* and *F* are chambers of respectively 150 cm.³ and 300 cm.³ capacity connected with the arms *M* and *N* of the differential, mercurial manometer. This manometer also served as a manoscope. The combination is the same as that used by Maneuvrier in his original work. The purposes of *E* and *F* are merely to give large volumes to the gas chambers of the manometer so that, in case a small leak should occur in either of these gas chambers, the rate of change of pressure in it should be negligible. *E* and *F* are separated by a stop-cock *S*₅ which in the final arrangement was not used. *G* is the compression chamber which contains the gas to be compressed or rarified. It has a capacity of about 300 cm.³ and is surrounded by a bath which contains a thermo-regulator and a stirrer (not shown in Fig. 5 nor in Plate I.). The volume of *G* can be increased or diminished at will by means of the device indicated at *O* which is actuated by compressed air. Chambers *B*, *C*, *E*, *F* and *G* are all japanned on the inner surfaces for the purpose of preservation and chamber *G* for the added purpose of surrounding the contained gas with a poor conductor for heat. *H* is a piston rod to which are clamped two stops *I* and *J* which are separated by a block of hard oak wood *K*. The use of different blocks of wood for *K* permits of different changes of volume in chamber *G* due to the thrusting in of the piston rod *H*. The lower stop *J* is firmly fixed to the rod *H* in order that, when *H* is in its lowest position, the volume of *G* is certain to be very closely a fixed amount. *V*₁ and *V*₂ are pin valves. *S*₁, *S*₂, *S*₃, *S*₄ and *S*₅ are stop-cocks. As already noted, *S*₅ was not made use of in the apparatus as finally arranged. The construction of *S*₃ is shown in Fig. 6. *S*₁, *S*₂, *S*₄ and *S*₅ differ from *S*₃ only in having the special device attached to the pin of *S*₃ replaced by a bar so that the pin may be rotated by hand. The pin of *S*₃ is rotated by a heavy weight *W* attached to a heavy spring which in turn is attached to a slender rope made of several strands of heavy fish-line, one end of which is wound about the wooden drum fastened to the pin of *S*₃. The pin of *S*₃ is provided with an arm *L* which serves



A. G. WORTHING.
PLATE I.

as a catch. The spring removes the sudden jolt that otherwise would be experienced on the sudden stoppage of the rotation of the pin of S_3 . The final ground surfaces of the pin and stock were produced by grinding them in powdered quartz and, sometimes, in pumice. In Fig. 5 a small tube is shown connecting C with P . The pressure in C was always nearly equal to that in the system $EFGMN$. Consequently this connection at P together with the packing about H permits at the most, of only a slow leakage of gas into or out of G through the packing and along the surface of H . Similar tubes lead from C to all the stop-cocks. They are connected to the stop-cocks at points which lead directly to the grooves Q (Fig. 6). These grooves entirely surround the pin of the stop-cock. As before the pressure in C is distributed through the tube to Q where it

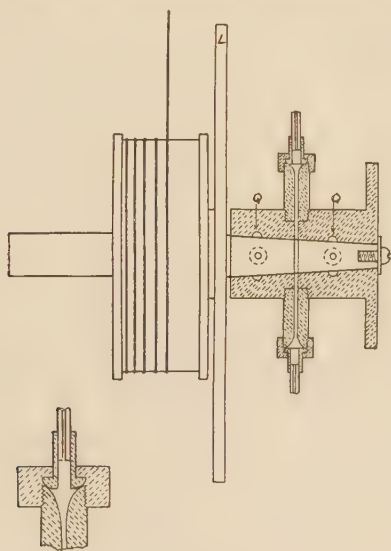


Fig. 6.

prevents the leakage of gas from or into the system $EFGMN$. The small tubing connecting the various chambers and stop-cocks is of copper. The external and internal diameters are respectively .32 cm. and .16 cm. The method of making the unions of these tubes with the other portions of the apparatus is well illustrated in Fig. 6. The external and internal diameters of the glass tubing used in the manometer are respectively .80 cm. and .30 cm. The stop-cocks are of brass, the chambers B , C , E , F and G were cut out of steel shafting.

In the method of experimentation pursued it was necessary to vary and to measure the time interval between the compression of the gas in G (Fig. 5) and the opening of the S_3 . This was brought about by means of the apparatus diagrammed in Fig. 7. The block of oak wood,

K (Fig. 5) carries a projecting metal prong *a*. The thrusting in or out of *H* brings *a* in contact with *b* and *c*. The contact *ab* closes an electrical circuit through the electro-magnet *d*, the energizing of which releases a pendulum which in its motion closes at *e* an electrical circuit through the electro-magnet *f*, opens at *g* the same circuit, and breaks at *h* by a device not indicated, the circuit containing the electro-magnet *d*. The current through the circuit closed at *e* actuates the electromagnet *f*, thus releasing the catch *L* attached to the pin of stop-cock *S*₃. The weight *W* causes the rotation of the pin of *S*₃. The breaking of the

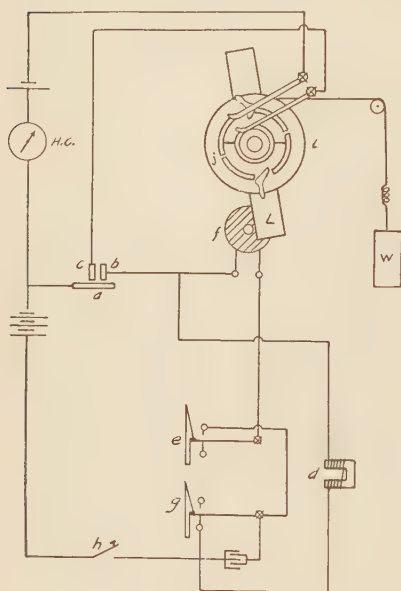


Fig. 7.

circuit at *g* is followed by the demagnetizing of *f*, and the catch *L*, after a rotation of the pin of 180°, is caught and the rotation of the pin is suddenly stopped. In case there is contact at *e* when the plunger *H* is moved in, the electromagnets in the circuits at *d* and *f* are actuated simultaneously. Thus by having the circuit at *e* initially closed or broken two different time intervals may be had between the compression of the gas in *G* and the opening of the cock *S*₃. Other intervals may be had by varying *W* and the position of *e* on the pendulum apparatus. The contact *ac* permits a current to flow through the commutation device on the drum *i* of *S*₃ through the electro-magnet of a Hipp's chronoscope

(H.C.). At *j* this current is broken when the stop-cock *S*₃ is open, as may be seen by inspecting the diagram of the commutating device. *S*₃ is diagrammed in a closed position. Thus the chronoscope records the time elapsing between the plunging in or out of *H* (Fig. 5) and the opening of the stop-cock *S*₃. Previous to July 28th, however, a slightly different method was used. The interval measured was from the plunging in or out of *H* to the closing of *S*₃.

Stop-cock Difficulties.—Originally it was planned to use tallow as the stop-cock lubricant, and to have the openings to *Q* and the grooves *Q* of the stop-cocks (Fig. 6) filled with gas directly connected with that in *C*. It was soon very evident that this plan must be abandoned. With this arrangement, pressures of a few atmospheres could be maintained for an hour at most. A great deal of time was spent in the search for some

stop-cock fluid which should be able to withstand the high pressures. The fluid finally used was formed by dissolving approximately one part of rubber in three parts of hot pine-tar. The solution was heated and the more volatile gases driven off until the desired consistency was reached. This fluid when cool is very viscous and sticky. It was introduced in the openings leading to Q and in the grooves Q . It did quite well and often for several hours, no noticeable leaks in the apparatus could be detected. With the very highest pressures the fluid was gradually forced out between the pin and the stock of the stop-cocks. However, there was no leakage of gas to the outside, until a complete passage-way to the outside for the gas back of the rubber-tar solution had been formed. As soon as such a passage-way was formed, the desired gas pressure in C was usually very hard to maintain by the admission of gas through S_1 and it was necessary to discontinue the experiment, empty the apparatus and refill the receptacles with the rubber-tar solution. For further work with this apparatus, considerably enlarged receptacles for the stop-cock fluid should be provided.

The Experimental Determination of Δp_Q .—In the filling of the apparatus with the gas to be experimented upon, it was necessary to be sure that the gas was dry and that whatever air was in the apparatus initially was removed or nearly so. The moisture was removed by the phosphorus pentoxide in B (Fig. 5). The phosphorus pentoxide was replaced by a fresh supply several times. In each instance, that furthest from the entrance to chamber B was found when removed to be a dry powder, thus indicating that in all cases the carbon dioxide gas experimented on was free from moisture. The removal of the air was accomplished partially with a hand pump, then carbon dioxide was allowed to fill the exhausted space. This mixture of air and carbon dioxide was then pumped out and the process repeated until it was certain that not more than .05 per cent. of the gas in the apparatus was of the original air. After the desired pressure throughout the apparatus including the protective system had been reached and had become steady due to the temperature having reached a steady state, S_3 was closed. Then, depending on whether the change in the compression chamber G was to be a compression or a rarefaction, the pressure in the protective system and in E and M was increased or decreased until the expected change in pressure in the compression chamber was equal to the difference indicated by the mercury levels in M and N . Then S_4 was closed. At this stage, it is to be kept in mind, the pressure in the compression chamber G was the same as that in F and that at the upper surface of the mercury in N ; and that the pressure in E was the same as that in M . Now with the rapid successive opening and closing of the valves letting compressed

air into and out from O , the gas in G was compressed or rarified due to the motion of the piston H , contact was made at ab and ac (Fig. 7), as explained above; the pin of S_3 was rotated connecting for a short space of time chambers E and G ; and the time interval between the making of the contact ac and the opening of S_3 was recorded by the Hipp's chronoscope H.C. This was very quickly followed by the reverse movement of the piston H in order that there might be but a very small amount of heat lost or gained by the gas in the compression chamber as a result of the heating or cooling from the previous direct motion of H . In case the pressures in G and M were not equal on the opening of S_3 , a passage of gas must necessarily have taken place through S_3 ; and, on the return of H to its initial position, S_4 was opened. There was a readjustment of pressure then in G , F , and N and also in E and M . When a steady state was reached, usually after a minute or so, the process beginning with the closing of S_4 was repeated. In fact it was necessary to repeat again and again until, by the automatic transference of gas through S_3 from G into E or vice versa, there should occur for at least for two successive repetitions no transference of gas from E to G or vice versa. This condition was determined by an observer looking through a cathetometer telescope at the upper mercury surface in M or in N . Whenever in the process described above there occurred a transfer of gas from G to E or vice versa, there was a shift in the mercury level. When a condition of balance obtained, no further shifting of the mercury surface could be noted, in fact no distortion of the surface could be detected. With the apparatus in working order, it usually did not require more than ten trials before the balance was obtained. The actual difference of pressure produced in the compression chamber and existing after the time interval shown by the Hipp's chronoscope, was measured on the differential manometer MN by means of the cathetometer. By varying the initial conditions at the contact e (Fig. 7), data corresponding to two time intervals may be obtained.

Now, if it may be assumed here that the change in *the change in pressure* due to heat being conducted to or from the gas in G is a linear function of the time for short intervals of time, we may obtain the change in pressure which would have occurred in G if the time interval had been infinitesimal. Let Δp_1 and Δp_2 be changes in pressure and Δt_1 and Δt_2 be the corresponding intervals of time in the above described experiment. Let Δp_0 be the change in pressure for an infinitesimal interval. Then we have

$$(45) \quad \Delta p_0 = \Delta p_1 - \frac{\Delta p_2 - \Delta p_1}{\Delta t_2 - \Delta t_1} \Delta t_1.$$

Δp_0 is the Δp_q of (44). Data from certain preliminary measurements obtained July 25 and platted in Fig. 8, indicate that the assumption is not far from true. Near the completion of the experimental work, other attempts were made to test (45) more carefully. In each instance, certain accidental changes occurred which made impossible the obtaining of the desired number of different intervals under conditions which would be necessary for a rigid test. Even if the assumption made is not true, the actual variation from it could hardly be such as to cause any serious error.

It is perhaps well to note here certain precautions taken to insure accuracy. The pressure gauge was always adjusted so that the index was aligned with some desired division on the dial. The face of the gauge was

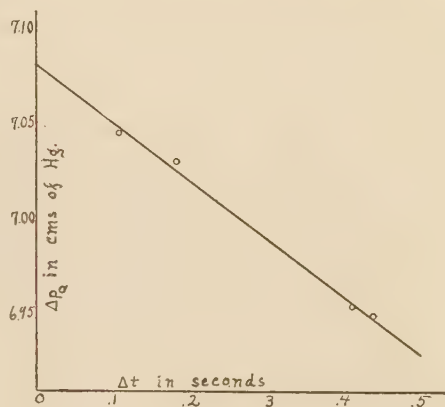


Fig. 8.

Experimental test of assumption made in (45)

always tapped lightly to insure the freedom of movement of the indicating parts. Parallax was carefully eliminated. A single division on the dial corresponded to $5 \frac{\text{lbs. wt.}}{\text{in.}^2}$. A variation of one twentieth

of a division was noticeable. This corresponds to about one sixtieth of an atmosphere. Actual trials showed that any desired pressure could be certainly obtained (assuming the gauge to be correct) to within 1.5 cm. of Hg. To prevent any errors due to the sticking of the mercury in the manometer tube, the glass tubes *M* and *N* were tapped just before and just after the compression or rarefaction in *G* was produced. To further eliminate such troubles, the initial pressure in *E* for one determination of Δp_q for a given *p* and *T* was first made too great and for the next determination under the same conditions was made too small, in order that in the self-adjusting process there would in the first case be a slight movement of the mercury in *N* upwards and then in the second case downwards. The two values of Δp_q obtained thus were always in very good agreement, they always differed in such a manner as to indicate that there was some sticking of the mercury to the manometer tubes. These differences in Δp_q , with a few exceptions relating to measurements especially difficult, did not amount to more than .6 mm. of Hg and usually were much less. The average of two such values for Δp_q were taken as

the observed value. When it is considered that the actual values of Δp_Q varied from 5 to 13 cm. of Hg, it will be seen that the uncertainties arising from this source will generally be quite small. In order to eliminate any errors in the measurement of Δp_Q due to leakage of gas during the measurements of the heights of the mercury columns in M and N , one observer noted during this process with the aid of a traveling microscope the slow motion, if it existed, of the mercury in column M . Corrections to the cathetometer readings for such leakages were readily made. In addition to the ordinary precautions for cathetometer work, double settings were made. If the readings from these double settings were not consistent with the difference noted on the traveling micrometer, further readings were taken.

In order that a clear idea of the method of procedure may be obtained, certain of the records for the afternoon of August 12 are presented in Table VIII., together with certain explanatory notes. C and R indicate

TABLE VIII.

*Sample note book records showing experimental details for determination of Δp_Q .
Aug. 12, 1910, P. M.*

Movement of compressing piston with blocks no. 3 and no. 4 at K (Fig. 4).

Mean of five determinations at the beginning

1.435 cm.

Mean of five determinations at the end

1.426 "

Av. 1.430 "

Gauge reading: $300 \frac{\text{lbs. wt.}}{\text{in.}^2}$.

Collected data:

Room Temp.	Bath Temp.	Change.	N in cm.	M in cm.	$M-N$ in cm.	Adjustment.	Interval in Sec.	Remarks.
26.6°	50.0°	C.	92.672	83.395	9.277	down	.095	?
.6	"	"	.658	.412	.246	up	.098	good
.6	"	"	.627	.430	.197	down	.070	good
.5	"	"	.610	.470	.140	down	.314	
.4	"	"	.630	.435	.195	up	.310	
.4	"	R	82.321	92.552	.231	up	.090	
.2	"	"	.340	.540	.200	down	.090	
.2	"	"	.365	.516	.151	up	.304	
.1	"	"	.390	.515	.125	down	.304	

Note book records from which N , M and interval entries of the fourth observation were taken.

N' in cm.	Chronoscope Reading.	Chronoscope Interval.	N'' in cm.	N in cm.	M in cm.	Traveling Microscope Reading in cm.
	005					
32.61	163	158	32.60	92.610		8.911
.60	322	159	.59	.605		15
.59	475	153	.59		83.480	19
.59	632	157	.59	Corrected 92.610	.480	21
					83.470	

respectively a compression and a rarefaction. The N and M readings are the cathetometer readings on the mercury menisci in tubes N and M (Fig. 5). $M \sim N$ represents the numerical difference between M and N . The adjustments "up" and "down" indicate that, in the self-adjustment of the gas pressure preceding the equilibrium, the motions of the mercury surface in N during a compression and in M during a rarefaction were "up" and "down" respectively. The "interval" measured is the time elapsing between the making of the circuit at ac (Fig. 7) and the breaking of the circuit at j . It is thus the interval between the plunging in of the piston H and the opening of stop-cock S_3 so that chambers E and G were in communication. Under remarks it is noted that the first observation was considered questionable when taken. It does not check up with the other observations from the standpoint of the variation in Δp_Q due to up and down adjustments. It has been discarded in the further computational work. The readings N' were read on a rough paper scale back of tube N with the aid of the cathetometer telescope, just before the gas in G was compressed; the readings N'' were taken in a similar manner just after. The unit of the chronoscope readings was .002 sec. The average interval was therefore .314 sec. The slight variations in the individual intervals are partially to be accounted for by the fact that the weight W (Fig. 5) was usually still being vibrated up and down somewhat by the spring above it when a new compression was about to be made. The method of obtaining the corrected N and M readings is evident. From the collected observations given, there are to be obtained as indicated above with the aid of (45) and on correcting $M \sim N$ to 0°C. , data recorded in the first six columns of Table XIII. under the proper date. Nearly all such data relating to Δp_Q represent values obtained in the manner indicated above, with the exception that usually only two observations, one an "up," the other a "down" for the same interval were taken either for the rarefaction or for the compression. In computing Δp_Q by (45), the term multiplying Δt , was assumed to be the same as in the other process for which the regular four observations were taken.

The Computations for Δp_Q .—Kamerlingh Onnes⁴¹ has given an empirical equation of state for CO_2 which is founded on Amagat's work and which represents Amagat's data with a very high degree of accuracy. The equation is of the form

$$(46) \quad \lambda p v = A + \frac{B}{\lambda v} + \frac{C}{(\lambda v)^2} + \frac{D}{(\lambda v)^4} + \frac{E}{(\lambda v)^6} + \frac{F}{(\lambda v)^8},$$

where

$$(47) \quad \lambda = \frac{p_c v_c}{\theta_c}, \quad p_c = \frac{p}{\pi}, \quad \theta_c = \frac{\theta}{\tau} \text{ and } v_c = \frac{v}{\nu},$$

in which α is the ratio of the two specific volume units, 1.00706. The term of (50) containing β is of the second order, consequently it is sufficient to have β approximately. Table X. gives such values to the nearest

TABLE X.

Values of β for equation (50).

P in Atmos	7.78	14.72	21.52	28.52	35.52	42.34	49.36	57.0
0° C.	.94	.88	.78	.66				
30	.96	.92	.87	.81	.74	.66	.55	.39
50	.97	.94	.90	.86	.82	.77	.71	.63
100	.98	.96	.95	.93	.91	.89	.87	.84

hundredth. Column 7, Table XI. contains the results of such computations for Δp_{θ} .

Calibrations and Miscellaneous Notes.—It should be noted here that various parts of the apparatus were carefully calibrated and measured. The differential surface tension effects in the manometer were always negligible. The changes in the density of the mercury due to the varying pressure were also found negligible. It was always to be noted on releasing the pressure in the apparatus that some CO₂ had been dissolved in the mercury. The amount was small, and, considering the limited amount of time at the writers' disposal, it never seemed sufficient to warrant an investigation. The possible effect of the dissolved CO₂ on the density of the mercury has been ignored. The pressure gauge was a Bowden steam test gauge of 800 $\frac{\text{lbs. wt.}}{\text{in.}^2}$ range. It was carefully calibrated. In determining the pressure of the gas in the apparatus account was taken of the barometric pressure. Throughout the time of experimentation this was .97 atmo. The thermometers were compared with standard thermometers. The volume of the compression chamber was obtained by finding the weight of the water necessary to fill it. The

TABLE XI.

Data for and results on γ for CO₂. Preliminary Results.

Date.	Temp. of Bath.	p in Atmos.	Change.	Piston Motion in cm.	Δp_{θ} in cm. of Hg.	Δp_{θ} in cm. of Hg.	γ	γ (corr.)	γ'	Purity of CO ₂ in %.
July 22	29.4	14.72	C	3.004	13.10	9.77	1.342	1.340		99.2
25	32.7	7.78	C	3.004	7.04	5.37	1.310	1.311		99.6
27	32.4	14.72	C	3.004	13.24	9.79	1.352	1.350		
30	32.2	28.52	C	1.422	12.09	8.04	1.503	1.508		
Aug. 1	31.0	7.78	C	1.422	3.348	2.529	1.324	1.325		
3	31.4	7.78	C	1.422	3.337	2.528	1.320	1.320		
4	31.8	7.78	R	1.422	3.326	2.507	1.326	1.327		
5	31.7	7.78	C	2.122	4.94	3.48	1.306	1.306		
5	31.4	7.78	C	2.122	4.97	3.78	1.314	1.315		

TABLE XI.—Continued.

Data for and results on γ for CO_2 . Final Results.

Date.	Temp. of Bath.	p in Atmos.	Change.	Piston Motion in cm.	Δp_Q in cm. of Hg.	Δp_g in cm. of Hg.	γ	γ (corr.)	γ'	Purity of CO_2 in %.
8	31.3	7.78	C	3.004	7.09	5.37	1.320	1.320	1.268	
9	30.8	7.78	R	3.004	7.01	5.32	1.317	1.317	69	
	31.5	14.72	R	3.004	13.20	9.71	1.359	1.360	63	
	32.2	14.72	R	1.422	6.18	4.60	1.344	1.346	50	
	31.7	14.72	C	1.422	6.23	4.61	1.352	1.353	51	99.6
10	31.2	28.52	C	1.428	12.05	8.09	1.488	1.489	50	
	31.8	28.52	R	1.428	12.14	8.06	1.505	1.509	63	
11	31.3	21.52	R	1.407	9.06	6.32	1.432	1.433	63	99.6
	31.2	21.52	C	1.407	9.09	6.34	1.434	1.434	62	
12	49.8	7.78	C	2.994	6.99	5.39	1.296	1.296	54	
	49.9	7.78	R	2.994	7.04	5.34	1.316	1.316	51	
	49.9	14.72	R	2.994	13.11	9.91	1.335	1.335	60	
	49.9	14.72	C	2.994	13.29	9.89	1.345	1.345	62	
	50.0	21.52	C	1.430	9.19	6.63	1.386	1.386	57	
	50.0	21.52	R	1.430	9.20	6.61	1.391	1.391	65	
13	50.0	28.52	C	1.421	12.15	8.39	1.448	1.448	61	
	50.1	28.52	R	1.421	12.10	8.37	1.447	1.447	64	
	50.2	34.52	R	.768	8.20	5.38	1.524	1.525	69	
	50.2	34.52	C	.768	8.16	5.39	1.515	1.516	62	
15	98.4	7.78	C	3.020	6.93	5.52	1.256	1.256	35	
	98.4	7.78	R	3.020	6.91	5.47	1.264	1.264	47	
	98.5	14.72	C	1.436	6.17	4.86	1.269	1.269	27	
	98.4	14.72	R	1.436	6.17	4.84	1.275	1.275	34	99.5
16	98.5	28.52	C	1.438	12.06	9.07	1.329	1.329	36	
	98.5	28.52	R	1.438	11.99	9.04	1.326	1.326	36	
	98.6	41.34	R	1.775	9.83	6.96	1.412	1.413	66	
	98.6	41.34	C	1.775	9.77	6.97	1.401	1.402	55	99.3
17	0.2	28.52	C	.786	6.49	3.83	1.694	1.694	48	
	0.2	28.52	C	1.425	11.91	6.95	1.710	1.710	34	
	0.2	28.52	R	1.425	11.81	6.94	1.702	1.702	32	
18	0.2	21.52	C	1.424	8.97	5.07	1.528	1.528	32	
	30.9	41.34	C	.786	9.93	5.61	1.771	1.770	59	
22	0.2	7.78	C	2.120	4.95	3.70	1.338	1.338	58	
	0.2	7.78	R	2.120	4.95	3.67	1.346	1.346	68	
23	98.6	34.52	C	.805	8.24	6.19	1.331	1.332	14	
	98.6	34.52	R	.805	8.27	6.18	1.339	1.340	24	
	98.6	48.36	C	.809	11.78	8.28	1.423	1.425	50	
24	31.6	7.78	C	4.388	10.31	7.88	1.309	1.309	57	
25	30.7	57.0	C	.798	13.78	5.85	2.36	2.35	82	
	31.1	7.78	C	3.038	7.12	5.43	1.310	1.310	58	

 γ (corr.) indicates values of γ corrected to the standard temperatures 0° , 31° , 50° and 98.5°C .

volume of the chamber and its accessories is 310.0 cm^3 . The average of 20 measurements of the diameter of the compressing piston gave 1.1098 cm . The purity of the gas was determined by bringing a known quantity of it into contact with KOH .

The time required for the thrusting in of the plunger H (Fig. 5) is a matter of some interest. If the thrusting in of the plunger and the reaching of a steady state by the gas could possibly occur in an extremely short interval such as .001 sec., one would need to give special consideration to the extremely high temperature gradient which would be established at the boundaries of the vessel. If, however, each of the two processes should take an appreciable time, no very high temperature gradient is to be expected at any instant. The time of inthrust of the plunger H was determined by taking the difference between two selected intervals. The first interval was from the starting of the plunger H to the opening of stop-cock S_3 , the interval being recorded in the manner described above by the chronoscope. The second interval differed from the first in that the contact beginning the interval was made near the end of the inthrust instead of at the beginning. The average of several such determinations showed that the time for the maximum inthrust was about .06 sec. In the measurements made this interval of inthrust was always included. Of course, for the smaller inthrusts, this interval was smaller.

Data and Results.—The data taken and the values of γ obtained are shown in Table XI. The values given may in a few cases differ by .001 from the quotient of Δp_q by Δp_θ because of the manner in which the former were obtained. The corrections for obtaining γ (corr.) for the four standard temperatures were obtained from an initial rough plat. The computed values of γ for these four standard temperatures have been platted in Fig. 9 as a function of the pressure. With a few exceptions, each platted point represents the mean of two determinations of γ , one from a compression, the other from a rarefaction. Two pairs of such values have been included in the point for the gas at 31° C. and a pressure of 7.78 atmospheres. The higher values were obtained early in the work. The lower values were obtained near the end. Sometime between August 18 and August 23, the date unfortunately not being recorded, the rubber washer between the compression chamber and its lid was replaced by a new one, which was noticeably thicker than the one removed. The importance of the consequent change in the volume of the compression chamber was not appreciated fully at the time or accurate measurements would have been taken. Account has not been taken of this change in the computations. However, if account should be taken of this change of volume, the separately determined values would more nearly coincide. The same is to be said regarding the values for γ at 98.5° C. for pressures of 35.52 atmospheres and 49.36 atmospheres. In this instance the values of γ taking account of the volume change

would also be raised so that the variations of the platted γ for this temperature would be less noticeable. The same possibility applies to γ for 0.2°C . at 7.78 atmospheres. It is to be noted that the preliminary values of γ , though not platted, agree very well with the final results.

Result of Maneuvrier and Results Based on C_v by Joly.—There is platted for comparison purposes the value of 1.298 determined by Maneuvrier,³⁷ the originator of this method, for CO_2 at atmospheric pressure and 10°C . Values of γ for CO_2 at atmospheric pressure have been rather discordant. Generally, however, such values approximate the results obtained here,

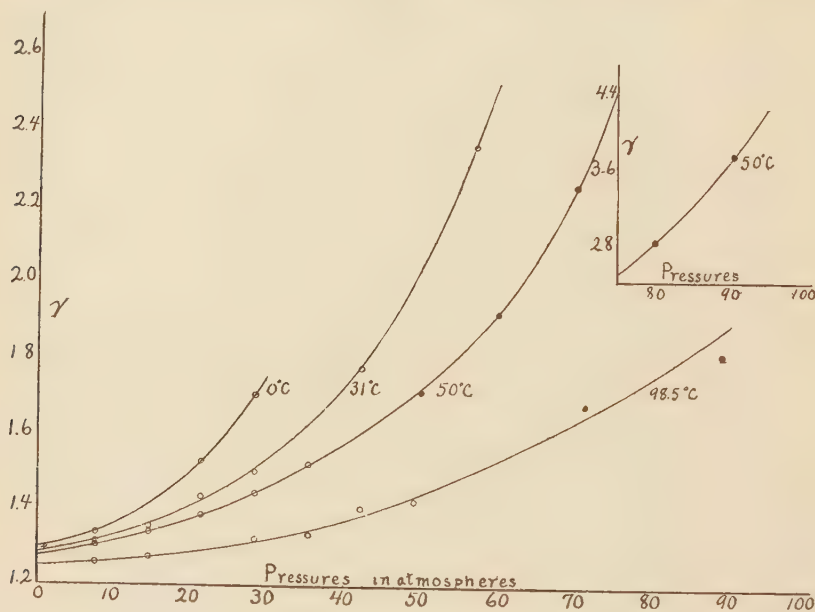


Fig. 9.

Variation of γ in CO_2 with pressure and temperature.

Results based on determinations

- | | |
|-----------------------------------|---|
| of C_v by Joly | ● |
| of Δp_a by Worthing | ○ |
| of Maneuvrier | + |

though the variation with temperature has been found to be less noticeable than what the writer has obtained. There are also platted values of γ which are based on determinations of C_v by Joly. The method of computing was that used by Amagat.³¹ Values of C_v and p, v, θ relations from the experimental data of Amagat were combined according to (13). This has been done by Amagat. The writer has not been able to verify fully the computations of Amagat and has here incorporated results from his own computations. The writer in determining $(\partial p / \partial \theta)_v$ and $(\partial v / \partial \theta)_p$

has used a graphical method. The values determined represent true values for the temperatures and pressures indicated. The values of C_v for pressures of 80 and 90 atmospheres at 50° C. have been taken from Amagat's extrapolation. The values for C_v at 100° C. result directly from equations given by Joly for CO₂ at densities .1240 gr./cm.³ and .1800 gr./cm.³ Table XII. includes these data and results. The general agreement is quite satisfying.

TABLE XII.

Data for and results on γ for CO₂ based on C_v determinations by Joly and p, v, θ determinations by Amagat.

T	p	C_v	$C_v \left(\frac{\partial v}{\partial \theta} \right)_p$	$-\left(\frac{\partial p}{\partial v} \right)_\theta$	C_p	γ
50° C.	50	.1920	.031310	2020	.329	1.710
	60	.2015	1280	2850	.386	1.915
	70	.2108	1345	3670	.474	2.245
	80	.2303	1530	4560	.644	2.83
	90	.2585	1800	5500	.945	3.73
100	71.3	.1902	0870	3690	.318	1.670
	87.8	.2056	0805	5590	.372	1.810

p is expressed in atmospheres, C_p and C_v in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$ and v in $\frac{\text{N. V. units}}{\text{gr. mol.}}$.

γ' of Equation $pv^{\gamma'} = \text{constant}$.—In the column (Table XI.) headed γ' are included values which are derived on the assumption that for the processes of compression and rarefaction considered, there holds the following relation:

$$(52) \quad pv^{\gamma'} = \text{constant.}$$

The approximate constancy of γ' for a given temperature is remarkable and is worthy of further experimental consideration. A γ' , of course, is not to be interpreted as a ratio of the two heat capacities except perhaps for the gas under zero pressure at the same temperature, or as described by the same adiabat, or under some other similar conditions. Differentiation of (52) and the application of (43) give

$$(53) \quad \left(\frac{\partial p}{\partial v} \right)_\theta = -\gamma' \frac{p}{v} = \gamma \left(\frac{\partial p}{\partial v} \right)_\theta.$$

Whence

$$(54) \quad \gamma = -\gamma' \frac{p}{v} \left(\frac{\partial v}{\partial p} \right)_\theta,$$

or according to Bakker³⁰

$$(55) \quad \frac{\gamma - \gamma'}{\gamma'} = -\frac{p}{v} \left(\frac{\partial v}{\partial p} \right)_\theta - 1 = \text{departure of gas from Boyle's law.}$$

Extrapolation to zero pressure, making use of these values of γ' , would seem to indicate that the platted curves of γ (Fig. 9), on being extrapolated back to zero pressure, had been extrapolated to too high values of γ . Not a great deal of dependence may be placed on this, however, until more is known about the function γ' .

Conclusions regarding γ and γ' .—The plats and tables show for CO_2 for the region considered:

1. The ratio of the two heat capacities γ for a given pressure decreases with an increase of temperature.
2. γ for a given temperature increases with pressure.
3. The curve for γ at 30°C . is such as to be consistent with the theoretical infinite value of γ at the critical point.
4. The agreement of the values based on Δp_Q data with those based on C_v data by Joly is very good.
5. The results at atmospheric pressure are in fair agreement with the results of others.
6. γ' , where $pv^{\gamma'} = \text{constant}$ applies to reversible adiabatic changes, is approximately constant.

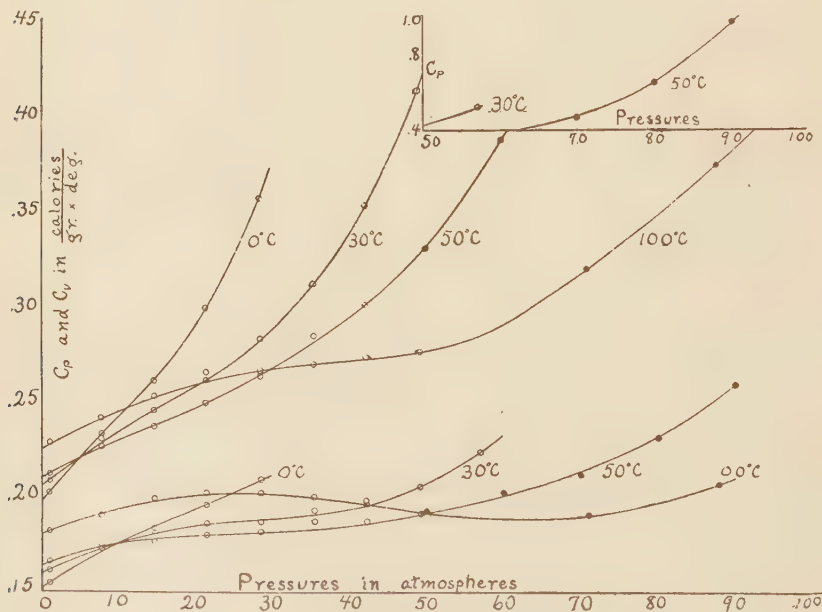


Fig. 10.

Variation of C_p and C_v of CO_2 with pressure and temperature.

Results based on determinations

- of C_p by Joly. ●
- of γ by Worthing. ○

V. DETERMINATION OF C_v AND C_p FOR CO_2 .

Determinations from the Present Work.—Equation (13) gives at once

$$(56) \quad (\gamma - 1)C_v = \theta \left(\frac{\partial p}{\partial \theta} \right)_v \left(\frac{\partial v}{\partial \theta} \right)_p.$$

This enables one to determine C_v and hence C_p by means of the data already obtained. The method of computation is evident. The transformation factor used in this work in the changing of the units of C_v and C_p to the ordinary units is expressed in (57).

$$(57) \quad 1 \frac{\text{atmos.} \times \text{N. V. unit}}{\text{gr. mol.} \times \text{deg.}} = 12.24 \frac{\text{cal.}}{\text{gr.} \times \text{deg.}}.$$

Values of C_v and C_p are to be found in Table XIII. Values of $(\partial p / \partial \theta)_v$, $(\partial v / \partial \theta)_p$ and $\theta (\partial p / \partial \theta)_v (\partial v / \partial \theta)_p$ are included in the hope that they may save some one otherwise extended computations. In Fig. 10 C_v and

TABLE XIII.

Data for and results on C_p and C_v of CO_2 .

T	p	γ	$\log \left(\frac{\partial p}{\partial \theta} \right)_v$	$\log \left(\frac{\partial v}{\partial \theta} \right)_p$	$\log \left[\theta \left(\frac{\partial p}{\partial \theta} \right)_v \left(\frac{\partial v}{\partial \theta} \right)_p \right]$	C_v	C_p	
0	7.78	1.342	.25130	.47359	.36852	.173	.233	
	14.72	1.418	.8459	.5156	.8856	.184	.261	
	21.52	1.528	1.0707	.4206	.9276	.196	.299	
	28.52	1.702	.2630	.3796	.20789	.209	.356	
	30	7.78	1.314	.24501	.7169	.36486	.174	.230
14.72		1.360	.7652	.4770	.7238	.180	.245	
21.52		1.420	.9680	.3545	.8041	.186	.265	
28.52		1.509	1.1315	.2778	.8909	.187	.282	
35.52		1.621	.2727	.2362	.9905	.193	.311	
	42.34	1.779	.3978	.2203	.20997	.198	.353	
	49.36	2.01	.5200	.2271	.2287	.205	.412	
	57.0	2.37	.6540	.2602	.3958	.223	.528	
	50	7.78	1.304	.24143	.7092	.36328	.173	.226
		14.72	1.340	.7208	.4620	.6921	.177	.237
21.52		1.386	.9159	.3291	.7543	.180	.249	
28.52		1.447	.30709	.2414	.8216	.182	.263	
35.52		1.521	.1997	.1826	.8916	.187	.284	
	42.34	1.603	.3100	.1441	.7964	.187	.300	
	100	7.78	1.260	.23401	.6966	.6085	.191	.241
		14.72	1.272	.6359	.4376	.6453	.199	.253
		21.52	1.291	.8188	.2920	.6826	.202	.261
		28.52	1.319	.9602	.1887	.7207	.202	.266
35.52		1.353	1.0750	.1127	.7595	.199	.269	
	42.34	1.392	.1699	.0551	.7968	.196	.273	
	49.36	1.44	.2561	.0089	.8368	.191	.275	

p is expressed in atmospheres, v in $\frac{\text{atmos.} \times \text{N. V. units}}{\text{gr. mol.}}$ and C_v and C_p in $\frac{\text{calories}}{\text{gr.} \times \text{degree}}$.

C_p are platted as functions of p . Values based on Joly's measurements (Table XII.) are included.

C_p Agreement with the Results of Others.—Very little agreement is to be found between the values of C_p here computed and the values of C_p obtained from a plat of Lussana's³³ results. The values of C_p for a pressure of one atmosphere as determined by the direct experiments of Holborn and Austin⁴² and by those of Swann⁴³ and as computed here are included in Table XIV. Excepting for the 100° C. value, the com-

TABLE XIV.

Values of C_p for CO₂ at atmospheric pressure expressed in $\frac{\text{cal.}}{\text{gr. } \times \text{deg.}}$

T	Holborn & Austin	Swann.	Worthing.
0	.203		.202
20		.202	
30	.207		.208
50	.210		.212
100	.216	.221	.228

puted results agree very well with the results of Holborn and Austin. At 100° C. the agreement is not good, though a better agreement is to be found with Swann's value for this temperature.

Causes for Possible Experimental Error.—Realizing early that the values for γ at 100° C. were slightly lower than was expected, special care was taken with the measurements. It is also, of course, an open question whether or not Kammerlingh Onnes's equation, which here bridges an experimental gap from 1 to 50 atmospheres and which here reaches its upper temperature limit of application, correctly represents the interrelations of p , v and θ for this region. The writer can not see how any experimental error in his work might produce this discrepancy. The supposition that the gas in the compression chamber has not all reached the temperature of the bath would lead to a discrepancy in the opposite direction, as would also the fact that a small amount of the gas, that in a portion of the connecting tubes, is at a considerably lower temperature than the bath. The possibility of local cooling next to the plunger during a compression might be thought to explain a part of the discrepancy. But that this is of small consequence is indicated by the good agreement obtained for γ by the rarefaction and by the compression measurements (Table XI.). Moreover, any such experimental error would be effective at the higher pressures, tending to produce too high values for C_v as well as C_p , an effect which is not in evidence in comparing the present results with Joly's (Figs. 9 and 10).

C_v Comparison with Joly's Results.—The attempt to compare the results on *C_v* computed above with the direct experimental values of Joly³² has not been as thorough as might be wished due to insufficient data. Joly concluded that the variations of *C_v* with temperature were very small for densities less than .08 gr./cm.³ for the temperature interval 0° C. to 100° C. The fact that his data do not strictly bear out his conclusion was ascribed to the observational inaccuracies entering in his work at the lower densities. This conclusion was accepted in the forming of Table VI. If it is fully accepted, very little agreement is to be found between the writer's values of *C_v* and those of Joly's. Moreover, it is not compatible with the results of Holborn and Austin and of Swann on *C_p* at one atmosphere and the ordinarily accepted variations of γ with the temperature for the same pressure. These would require that at atmospheric pressure *C_v* should increase noticeably with temperature, a variation just the opposite of that found by Joly for the higher pressures. The writer has assumed that the apparent disappearance of a temperature effect with decreasing densities in Joly's results might have been a disappearance preparatory to a reversal of the temperature effect, and has computed from Joly's individual results what the values of *C_v* would be for certain densities and temperatures if the results were correct. In doing this Joly's equation for *C_v* at a density of .124 gr./cm.³ has been used. For the densities .0800 gr./cm.³ and .0456 gr./cm.³ values of *C_v* were obtained by the deriving of an equation holding over a portion of the temperature range in a manner similar to that used by Joly. Other values of *C_v* were obtained by a quadrature method based on the general principle that

$$(58) \quad C_v = \frac{\partial}{\partial T} \left[\bar{C}_v(100 - T) \right]_v,$$

where $\bar{C}_v$ is the mean value of *C_v* between *T* and 100° C. These results with corresponding values obtained from the writer's work are included in Table XV. The table indicates a fair agreement between the results

TABLE XV.

Corresponding values of C_v as determined by Joly and by Worthing.

<i>T</i>	<i>p</i>	<i>C_v</i> (Joly.)	<i>C_v</i> (W.)	<i>p</i>	<i>C_v</i> (Joly.)	<i>C_v</i> (W.)	<i>p</i>	<i>C_v</i> (Joly.)	<i>C_v</i> (W.)
0°	19.4	.194	.193						
30	22.6	.178	.186	36.0	.189	.193	49.0	.208	.205
50	24.6	.170	.181	40.0	.185	.186			
100	29.5	.206	.202	49.0	.200	.192			

p is expressed in atmospheres, *C_v* in $\frac{\text{cal.}}{\text{gr.} \times \text{deg.}}$.

of Joly thus interpreted and the writer's. As suggested above, insufficient data may account for a part of the actual variations.

Conclusions Regarding C_v and C_p .—For the region considered in CO_2 , the following conclusions may be drawn:

1. The isometric heat capacity of CO_2 , C_v , at low pressures increases with increasing temperature. The reverse is true for sufficiently high pressures.
2. For a given temperature C_v generally increases with increasing pressure. The reverse is true for a certain pressure interval at 100°C .
3. There is a good agreement between the results on C_p obtained by the writer and those obtained by Joly.
4. The isopiestic heat capacity C_p at low pressures increases with increasing temperature. The reverse is true for sufficiently high pressures.
5. For a given temperature C_p increases with increasing pressure.
6. The variation of C_p at 30°C . is such as to be consistent with a theoretically infinite value at the critical point.
7. At atmospheric pressure the computed values of C_p agree well with the experimental values of Holborn and Austin and of Swann.
8. At high pressures the values found using the writer's experimental results are such as to be consistent with results based on Joly's data on C_v .
9. Very little agreement has been found between the writer's results and Lussana's results.

VI. THE FREE-EXPANSION AND JOULE-KELVIN EFFECTS IN CO_2 .

Results.—The methods of computation were those detailed in connection with the free-expansion and Joule-Kelvin effects in air. The results are to be found in Table XVI. Results for pressures of 50 atmospheres and higher for 50°C . and 100°C . have been determined by taking the results of Joly on C_v , the individual values being taken from the curves of Fig. 10. A value for both μ and η at the critical point ($p = 72.9$ atmos., $\theta = 304.5^\circ \text{K}$.) has been obtained by Keesom⁴⁴ by measuring the $dp/d\theta$ of the vapor tension curve of CO_2 at that point. Theoretically at the critical point of a substance there exists but a single value for $dp/d\theta$. This follows at once from (8), since at this point $(\partial p/\partial v)_\theta = 0$. Consequently we have

$$(59) \quad \mu_c = \eta_c = \left(\frac{d\theta}{dp} \right)_c$$

where the subscript c indicates the critical point values. These values of μ and η are included in Table XVI. The results as functions of the

TABLE XVI.

Data for and results on μ and η for CO_2 . Results based on K. Onnes's equation and on γ data by Worthing.

T in $^{\circ}\text{C.}$	p in Atmos.	$\theta - v \left(\frac{\partial \theta}{\partial v} \right)_p$ in $^{\circ}\text{K.}$	$\theta \left(\frac{\partial p}{\partial \theta} \right)_v - p$ in Atmos.	μ in deg./atmo.	η in deg./atmo.	$\frac{\Delta W_1}{\Delta W_2}$
0	7.78	48.8	1.12	1.398	1.266	.144
	14.72	87.9	4.44	1.333	1.259	.302
	21.52	125.9	10.62	1.334	1.262	.494
	28.52	161.3	21.52	1.329	1.265	.750
30	7.78	38.3	.76	1.084	.979	.098
	14.72	69.5	2.93	1.051	.978	.199
	21.52	99.7	6.64	1.063	.989	.309
	28.52	128.3	12.51	1.054	.993	.440
	35.52	157.0	21.28	1.059	1.008	.600
	42.34	183.6	33.42	1.061	1.023	.790
	49.36	209.4	51.04	1.048	1.023	1.035
	57.0	235.2	79.67	.995	.985	1.40
50	7.78	33.3	.61	.926	.833	.078
	14.72	60.3	2.27	.901	.827	.154
	21.52	86.5	5.10	.905	.836	.237
	28.52	112.4	9.52	.912	.854	.334
	35.52	136.5	15.65	.914	.868	.440
	42.34	158.8	23.62	.905	.870	.560
100	7.78	24.3	.38	.618	.557	.049
	14.72	44.3	1.41	.587	.537	.096
	21.52	63.9	3.06	.586	.530	.142
	28.52	82.5	5.52	.586	.539	.194
	35.52	100.4	8.82	.591	.553	.249
	42.34	116.7	12.84	.596	.565	.304
	49.36	133.1	17.96	.604	.583	.364

Results Based on C_p Data by Joly and p, v, θ Data by Amagat.

50	50	183	35.6	.895	.865	.713
	60	212	58.0	.860	.850	.980
	70	240	89.8	.835	.835	1.28
	80	265	145.5	.765	.780	1.82
	90	286	230.0	.655	.670	2.62
100	71.3	190	48.4	.635	.660	.68
	87.8	221	80.2	.585	.615	.92

Results Based on $d\mu/d\theta$ at Critical Point by Keesom.

31	72.9	304	416.	.622	.622	5.71
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closely to the drawn curves. The variations here are such as would indicate that for good agreement of the results among themselves, the values of γ for the lower pressures should be somewhat less than they have been indicated to be. This is in exact conformity with the indications derived above in considering γ' of (49). However, the smallness

pressure and the temperature are platted in Fig. 11. Excepting for the values at zero pressure and at 7.78 atmospheres, the points lie very of the terms $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$ for low pressures might well account for the variations in μ and η in such cases.

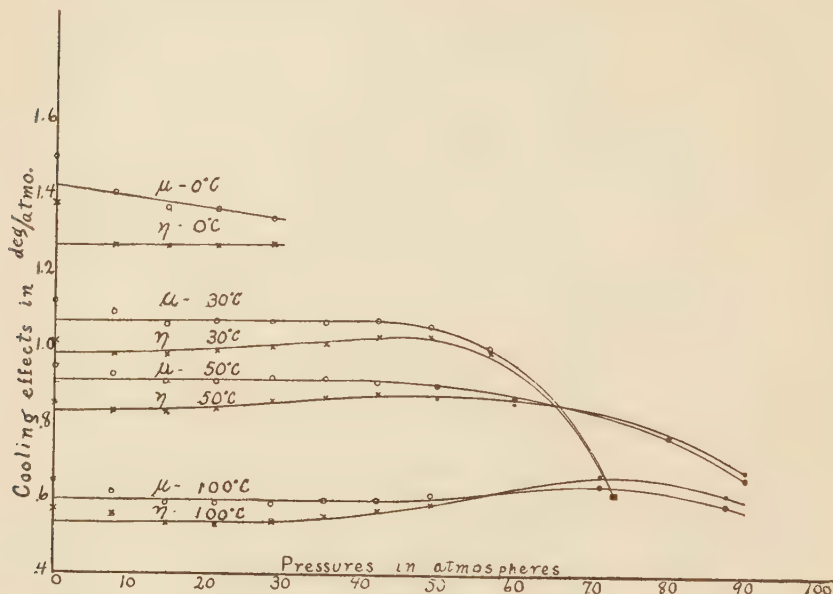


Fig. 11.

Variation of the free-expansion (η) and the Joule-Kelvin (μ) effects in CO_2 with temperature and pressure.

Results based on determinations of

C_p by Joly.....	●	■
γ by Worthing.....	○	×
$\frac{dp}{d\theta}$ by Keesom.....	■	

Results for Low Pressures.—In Fig. 12 there have been platted μ and η as functions of the temperature for the gas under low pressures. There have been indicated also the results of Kester,¹⁴ Joule and Kelvin,⁹ Natanson¹³ and some other observers. The non-agreement of μ and η at zero pressures with values at the higher pressures led the writer to consider the application of data by Chappuis⁴⁵ on the p , v and θ interrelations and data on C_p by Holborn and Austin. Chappuis's results are expressed in equations of the form

$$(60) \quad pv = A + Bp$$

for five different temperatures, -17.5° , 0° , 20° , 40° and 100° C. A and B are constants. The unit of pressure used is that due to a meter

column of mercury, the unit of volume is that occupied by a gram-molecule of the gas, at 0° C., under a pressure equal to that due to a meter column of mercury. In a method exactly analogous to that used in obtaining (27) and (28), we get for $p = 0$

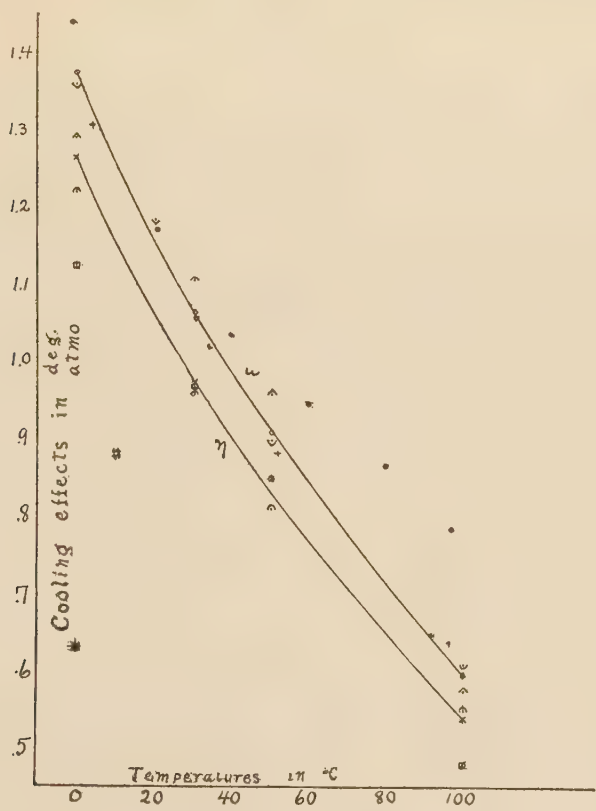


Fig. 12.

Variation with temperature of the free-expansion (η) and the Joule-Kelvin (μ) effects in CO₂ at low pressures.

Determinations of Joule-Kelvin effects

- by Joule and Kelvin..... +
- by Natanson..... ∇
- by Kester..... •
- from data by Chappuis and by Holborn and Austin..... $\triangle$
- from Clausius's equation..... $\circ$
- by Worthing..... $\bigcirc$

Determinations of free-expansion effects

- by Cazin..... #
- by Searle..... *
- from data by Chappuis and by Holborn and Austin..... $\square$
- from Clausius's equation..... $\odot$
- by Worthing..... $\times$

$$(61) \quad \mu_0 = \frac{\theta \left(\frac{\partial B}{\partial \theta} \right)_p - B}{C_p},$$

$$(62) \quad \eta_0 = \frac{\theta \left(\frac{\partial B}{\partial \theta} \right)_p}{C_p - \frac{A_0}{\theta_0}},$$

where A_0 and θ_0 are the values of A and θ for 0° C. (61) and (62) are based on the assumption that

$$(63) \quad A = A_0 \frac{\theta}{\theta_0},$$

a condition which is necessary if the gas in question is to approach the condition of a perfect gas as the pressure approaches zero. Chappuis's constants do not quite fulfil condition (63). Slight changes were made in his values for A and B , leaving the values for A and B at 0° C. and the values of $p\theta$ at the unit of pressure unchanged, such that condition (63) was fulfilled. This seems reasonable, in view of the added fact that, of the measurements by Chappuis at three different pressures, the average pressure was about equivalent to that due to a meter column of mercury. Thus changed B is readily and with a great deal of accuracy expressed by the following empirical formula,

$$(64) \quad 10^5 B = -906 + 6.87T = .0226T^2.$$

Chappuis's value for A_0 is 1.00906. The values indicated as being based on data by Chappuis and by Holborn and Austin, were obtained under the above named conditions. Some check computations for μ and η at 1 m. of Hg pressure based on quadrature methods and using Chappuis's constants unchanged showed excellent agreement with the values obtained using the modified constants of (63) and (64). To obtain values of C_p at zero pressure Holborn and Austin's data were used in conjunction with the change for one atmosphere indicated by the curves in Fig. 10. The results indicated as being based on Clausius's equation were obtained for zero pressure by a method analogous to that used in obtaining (27), and (28), and (61) and (62). Clausius's⁴⁶ equation and the numerical values of the constants are given in (65).

$$(65) \quad p = \frac{R\theta}{v - a} - \frac{c}{\theta(v + b)^2}$$

$$R = .003688,$$

$$a = .000843,$$

$$b = .000977,$$

$$c = 2.0935.$$

The resulting values for μ and η at zero pressure are

$$(66) \quad \mu_0 = \frac{\gamma - 1}{\gamma} \left(\frac{3c}{R^2\theta^2} - \frac{a}{R} \right),$$

$$(67) \quad \eta_0 = \frac{2c(\gamma - 1)}{R^2\theta^2}.$$

The curves of Fig. 9 furnished the desired values of γ . The value found by Searle⁸ was obtained through considering the application of Van der Waal's equation. The value by Cazin⁷ is an average of the four values .81, .82, .82 and 1.09 deg./atmo. which are obtainable from his results. The method is briefly described in the introduction. The first value is directly obtainable from his results. The other values are obtained indirectly. In obtaining his results for these three cases, Cazin had the larger chamber, into which the gas experimented on expanded from a smaller chamber, partially filled with the gas. In arriving at the above values, the rough assumption was made that the gas freely expanding was that in the smaller chamber in excess of the amount necessary to produce it in a pressure equal to the pressure existing in the larger chamber.

Note Regarding Disagreement of Values at Zero Pressure.—The high values of μ and η for $p = 0$ using Kammerlingh Onnes's equation (Fig. 12), are offset by the results based on the careful work of Chappuis and the work of Holborn and Austin and the results obtained with the aid of Clausius's equation. The difference arises from small variations in the p, v, θ relations. This disagreement might seem to cast doubt upon the values for the higher pressures. This is not necessarily the case, however, for with increasing pressure, as mentioned before, small errors in the p, v, θ relation become less effective due to the relative increase in size of the terms $\theta - v(\partial\theta/\partial v)_p$ and $\theta(\partial p/\partial\theta)_v - p$.

Internal Work during Expansion.—As in the case with air, it is of interest to consider the relative magnitude of the internal work on expansion when compared with the external work. (35) gives this relation for an infinitesimal, reversible, isothermal expansion. Values of $\frac{\Delta w_1}{\Delta w_2}$ are included in the final columns of Table XVI. The results, excepting the value 5.71 for the critical point, have been platted in Fig. 13. The platted points fall very closely on the smoothed curves. The effects of temperature and pressure are well shown. This plat incidentally shows very plainly the cause for the high values for γ at the higher pressures. In determining the isopiestic heat capacity of a gas, one neces-

sarily must consider the internal work of expansion, a factor which does not enter into the isometric heat capacity. Consequently there are relatively large values of γ , where the values of $\frac{\Delta w_1}{\Delta w_2}$ are relatively large. This relation is further borne out by the striking similarity of the two plats.

Conclusions Regarding and $\mu, \eta, \frac{\Delta w_1}{\Delta w_2}$ for CO_2 .—The following conclusions

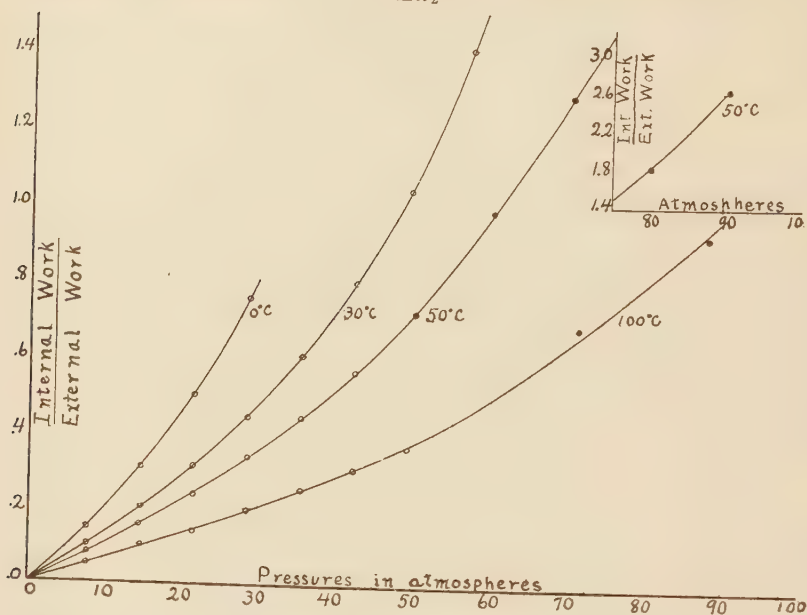


Fig. 13.

Variation with pressure of $\frac{\text{internal work}}{\text{external work}}$ for reversible, infinitesimal, isothermal expansions in CO_2 .

Results based on determinations of

C_v by Joly..... ●
 γ by Worthing..... ○

sions for CO_2 for the regions considered may be drawn from the plats of μ, η and $\frac{\Delta w_1}{\Delta w_2}$.

1. For pressures up to about 60 or 70 atmospheres the free-expansion effect is less everywhere than the corresponding Joule-Kelvin effect. For the higher pressures the reverse is true.

2. For pressures up to about 60 or 70 atmospheres the values of μ and η decrease with increasing temperatures for the temperature interval 0° to 100°C . For sufficiently high pressures there is a reversal of this temperature effect.

3. μ for a given temperature is approximately independent of the pressure up to about 40 atmospheres. For higher pressures (excepting at 100° C.) it decreases with increasing pressure.

4. η for a given temperature is nearly constant with varying pressure up to about 30 atmospheres. With increasing pressures η first increases slightly, then decreases more rapidly.

5. There is general good agreement among the μ and η determinations based on the different experimental data.

6. The writer's computed values for μ at moderate pressures agree very well with the experimental values of Joule and Kelvin and with the values obtained by using Clausius's equation, but are consistently less than the results of Kester.

7. The writer's values for η show excellent agreement with the values to be computed on making use of Clausius's equation.

8. The ratio of the internal work to the external work for infinitesimal, reversible, isothermal expansions $\frac{\Delta w_1}{\Delta w_2}$ is greater for a given pressure the lower the temperature.

9. The ratio $\frac{\Delta w_1}{\Delta w_2}$ starts with zero values at zero pressure and increases with pressure, reaching a value of 5.71 at the critical point.

VII. SIGNIFICANCE OF A NOTICEABLE RELATION BETWEEN μ AND η FOR AIR AND FOR CO_2 .

It is to be noticed that the results for μ and η for air and CO_2 show some marked differences. Among them is the fact that η is greater than μ in air for the region considered, while the reverse is true for a large portion of the region considered in the case of CO_2 . A brief discussion of this fact may perhaps bring out the significance of this. Consider Fig. 14 in which POQ represents an isothermal platted on a (pv, p) diagram. Consider some gas to be in a state represented by O on the diagram and about to be expanded through a porous plug. On the diagram, the path representing the change will evidently proceed from O to some point to the left of mn ,

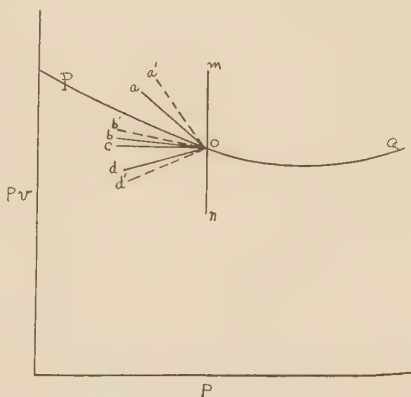


Fig. 14.

an isopiestic through O . In case the path should be along Ob , Oc or Od , cooling of the gas would occur and a positive Joule-Kelvin effect, as in air or in CO_2 , would be evidence. In case the path should be along Oa , heating of the gas would occur and a negative Joule-Kelvin effect as in hydrogen would be evidenced. The condition necessarily fulfilled in a porous plug expansion is

$$(68) \quad \Delta\epsilon + \Delta(pv) = 0.$$

The condition necessarily fulfilled in a free-expansion is

$$(69) \quad \Delta\epsilon = 0.$$

According to conditions, for instance whether in Fig. 14 the path proceeds from O into the upper left hand quadrant, along Oc , or into the lower left hand quadrant, we have respectively for the porous plug expansions

$$(70) \quad \Delta(pv) > 0, \quad \Delta(pv) = 0, \quad \Delta(pv) < 0.$$

For these cases we also have respectively

$$(71) \quad \Delta\epsilon < 0, \quad \Delta\epsilon = 0, \quad \Delta\epsilon > 0.$$

In the first case, where the path representing the porous plug expansion proceeds into the upper left hand quadrant and for which $\Delta\epsilon < 0$, the path for a free-expansion, in which $\Delta\epsilon = 0$, lies above that for the porous plug expansion. Hence, taking into account the signs of the effects, the free-expansion effect is less than the Joule-Kelvin effect.

In the second case, where the path representing the porous plug expansion proceeds along Oc and where $\Delta\epsilon = 0$, the path for a free-expansion also proceeds along Oc . Here the two cooling effects are equal.

In the third case, where the path representing the porous plug expansion proceeds from O into the lower left hand quadrant and for which $\Delta\epsilon > 0$, the path for a free-expansion in which $\Delta\epsilon = 0$, lies below that for the porous plug expansion. Here the free-expansion effect is greater than the porous plug effect. The converse of these statements is also true.

In the regions considered in air and in CO_2 we have for the most part portions of isothermals which when represented on diagrams as in Fig. 14 correspond to the portion PO . In air where the Joule-Kelvin and free-expansion effects are both positive and the latter the greater, we have porous plug expansions and free-expansions whose paths would correspond respectively to Od and Od' . For CO_2 at the lower pressures, where the Joule-Kelvin and free-expansion effects are both positive and

the latter the smaller, the corresponding paths are Ob and Ob' . At somewhat higher pressures where the two effects are equal, the corresponding paths coincide and lie along Oc . At still higher pressures where the two effects are reversed, we have conditions existing as described above in air.

VIII. SUMMARY.

1. An expression has been developed which shows clearly the relation between the free-expansion effect η and the ratio of the two heat capacities γ of a substance.

2. With the aid of γ data by Koch, $p v \theta$ data by Witkowski and an empirical equation of state by Kammerlingh Onnes, there have been computed values for the free-expansion effect η , the Joule-Kelvin effect μ and the ratio of the internal work to the external work for infinitesimal reversible, isothermal expansions $\frac{\Delta w_1}{\Delta w_2}$ for air at 0° C. and at -79.3° C. and for pressures up to 130 atmospheres.

3. With the aid of Kammerlingh Onnes's equation of state, there have been obtained experimentally by Maneuvrier's method values of γ for CO_2 at 0.0° , 31.0° , 50.0° and 98.5° C. and for pressures ranging from about 8 atmospheres to 57 atmospheres.

4. The approximate constancy of a new function γ' where γ' is defined by $p v \gamma' = \text{constant}$ —for CO_2 has been pointed out.

5. Values for the isometric heat capacity C_v , the isopiestic heat capacity C_p , μ , η and $\frac{\Delta w_1}{\Delta w_2}$ for CO_2 at 0° , 30° , 50° and 100° C. and for pressures—making use of C_v data by Joly—up to 90 atmospheres have been computed.

6. The results of the present work have been shown to be generally in good agreement with the experimental results of others.

7. A discussion has been presented in which certain characteristics of the expansions of air and of carbon dioxide through a porous plug and into a vacuum are considered.

The conclusions reached regarding the variations of the various quantities considered will be found summarized at the close of the different subdivisions of the present paper.

In conclusion, I wish to express my sincere thanks to Mr. R. E. Miller for care shown in the construction of the apparatus, to Mr. C. E. Guthe, Jr., for efficient aid given in the experimental work, and especially to Dr. K. E. Guthe for his kindly interest and helpful suggestions.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.,
March, 1911.

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ERRATA AND ADDENDA.

Page 259. To enable one to locate properly points platted in Fig. 12 in the paper by A. G. Worthing on Some Thermodynamic Properties of Air and of Carbon Dioxide, the following table is given:

μ and η for CO_2 at low pressures.

μ in Atmos.	T in °C.	μ in Deg./Atmos.	η in Deg./Atmos.
Results of Joule and Thomson.			
1- 6	4.0	1.307	
	33.5	1.020	
	51.9	.883	
	91.8	.648	
	96.0	.639	
Result of Cazin.			
1- 5	10		.88
Result of Natanson.			
	19.7	1.18	
Results of Kester.			
1-40	.6	1.442	
	20.4	1.173	
	39.5	1.037	
	59.5	.948	
	79.5	.868	
	96.6	.786	
Result of Searle.			
5-10	0		.63
Results of Worthing.			
0	0	1.375	1.265
	30	1.065	.975
	50	.910	.830
	100	.595	.540
Results based on data by Chappuis and by Holborn and Austin.			
0	0	1.290	1.125
	30	1.108	.970
	50	.960	.850
	100	.575	.480
Results based on Clausius's equation and γ data by Worthing.			
	0	1.36	1.22
	30	1.06	.96
	50	.90	.81
	100	.61	.55

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